ANNUAL PROGRAM REVIEW

CORROSION CONTROL

March 8, 2000

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Revised 02/16/00:at

DUES-FUNDED PROJECT SUMMARY

Project Title:	**Recovery Boiler Corrosion**
Project Number:	**F018**
PAC:	**Corrosion Control**
Project Staff	
Principal Investigator:	**Preet Singh**
Co-Investigators:	**Safaa Al-Hassan, Greg Fonder**
Research Support Staff:	**Jamshad Mahmood**
PAC Subcommittee	**N/A**
FY 99-00 Budget:	**$107,355**
Allocated as Matching Funds:	**30%**
Time Allocation:	
Principal Investigator:	**15%**
Co-Investigator:	**65%, 10%**
Research Support Staff:	**10%**
Supporting Research:	
Special Students:	**N/A**
External (Where Matching Is Used):	**Project 4111 (DOE)**

RESEARCH LINE/ROADMAP:
Research Line #9 - Reduce lifetime costs of construction by 30% through innovative technologies

Research Line # 8 - Improve operation and control of current recovery boilers

PROJECT OBJECTIVES:
Improve safety and increase operating life of kraft recovery boiler equipment by understanding corrosion mechanisms, properly selecting construction materials, and identifying suitable process conditions.

PROJECT BACKGROUND:
It is known that corrosion rates can be very different in different areas of the lower furnace in kraft recovery boilers. Generally, an area with a low corrosion rate can be adjacent to anarea with higher corrosion rate. If construction material for the waterwall tubes in these two areas is the same, then the differences in corrosion rate can be attributed to different environmental conditions in the two areas. The main objective of this project was to identify these differences and the reasons for these variations.

A B&W boiler (Boiler #1) that had areas with different corrosion rates was selected for initial study under a DOE/DF project. This boiler was equipped with two oscillating liquor guns that sprayed black liquor at the sidewalls of the boiler. Gases were sampled from specially installed ports and analyzed online using a gas chromatograph designed specifically for this application. Analysis of gases and temperature data has indicated that the corrosion rates were different due to the differences in the local gas composition at waterwall surfaces in the two selected areas. Differences in the local gas composition were due to liquor firing practices by which the black liquor is intentionally sprayed on to the sidewall. Local pyrolysis of black liquor on the waterwall surface leads to higher concentrations of sulfur-bearing gases in these areas of the wall. Local high concentrations of sulfur-bearing gases lead to higher sulfidation or corrosion of carbon steel waterwalls in these areas. However, in the adjacent areas where the liquor does not pyrolyze at the waterwall surface, the rates of corrosion were found to be lower. Gas analysis correlated very well with the mill's annual ultrasonic waterwall thickness data. Details of this study were included in 1999 annual project review report.

Based on the above-stated results, it was recommended by the PAC, during the 1999 spring meeting, that similar environmental characterization should also be carried out in other boilers with different liquor spray patterns and firing practices. A B&W boiler (Boiler #2) with similar design to Boiler #1, but with different firing practices, was selected for the present study. In this boiler, black liquor is sprayed in the center of the boiler but is not intentionally sprayed on the waterwall surfaces. This report will describe some major findings from this work. Conclusions at the end are based on overall work from the two boilers monitored so far.

DELIVERABLES:

Any water leak in the recovery boiler can potentially cause a boiler explosion. Therefore corrosion monitoring and control of waterwall tubes is very important for safe operation of kraft recovery boilers. Results from this project will benefit the industry in the following ways.

- Provide an understanding of local environments in the recovery boilers and their impact on the corrosion of recovery boiler waterwall tubes to help us select cost-effective construction materials for safe recovery boiler operation.
- Reveal operating conditions that may be varied to control waterwall corrosion without affecting boiler efficiency.
- Provide an understanding of corrosion mechanisms in kraft recovery boiler furnaces to help us improve risk analysis and life prediction of these boilers.

STATUS OF GOALS FOR FY 1999-00:

1. Characterize the corrosive environments in Boiler #2 by July 1999. It was done and preliminary work was discussed with the PAC during the Fall 1999 meeting.
2. Prepare a detailed experimental plan for the laboratory verification of corrosion and present it to the PAC during the Fall 1999 meeting. It was completed and approved by the PAC to be finished by June 2000.
3. Verify in the laboratory that carbon steel corrosion rates are due to the gas species and concentrations found in operating Boiler #1. Compare mill data with the lab results. To be finished by June 2000.

SCHEDULE:

Task Descriptions	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
Installation of sampling ports in boiler # 2	-------X				
Online characterization of corrosive environment	-------	--X			
Data analysis	-- -	---------X			
Determination of various ways to carry RB Gases to labs for characterization instead of on-line chromatograph		---------- -	---------X		
Conduct coupon exposure tests with and without water vapors			----	----------	X
Report results to member Companies					**Fall PAC Meeting**

SUMMARY OF RESULTS:

Sampling ports were installed in Boiler #2 during the mill's annual shutdown. these included ports to characterize temperature, gas composition, and smelt composition. In July 1999, monitoring equipment including a gas chromatograph was shipped to the mill and researchers spent roughly two weeks in the mill collecting relevant data.

Results from this study have confirmed that the gas composition at the waterwall surface can be very different from the bulk gases. However, gases at the waterwall surface that come in contact with the waterwall material are of the most significance as they participate in corrosion reactions on the metal surface. Gas composition at the waterwall surface depends upon operating parameters such as firing practices and overall gas flow patterns inside the boiler.

Temperature measurements in two selected areas have indicated that the waterwall surface temperature is very close to the saturated steam temperature. There was no measurable temperature difference in two selected areas, even though one area was in the corner of the boiler and the other was in the middle of the waterwall, near the liquor gun.

Boiler #2 has a studded waterwall till tertiary airport. There was indication that a thin frozen smelt layer was covering the waterwall surfaces in both selected areas. However, there was no apparent difference in the smelt layer thickness or quantity of frozen smelt in the two areas. Smelt samples could not be collected for composition analysis; however, the composition in the two areas is not expected to be different enough to affect corrosion.

SUMMARY OF KEY CONCLUSIONS:

1. Results from this investigation have indicated that there is no temperature difference in the two selected areas in Boiler #2.
2. There was evidence of smelt in both selected areas, but the smelt samples could not be extracted through installed ports. However, the smelt compositions in the two areas are not expected to be different.
3. In Boiler #2, where the liquor is not intentionally sprayed on the waterwalls, gaseous environments in the two selected boilers are very similar. Based on these results one can predict that the waterwall corrosion rates will be low and very similar in the two selected areas of Boiler #2
4. Gases at the waterwall surface are very different from the bulk gases in the lower furnace of the kraft recovery boilers.
5. Results from this study (Boiler #1 and Boiler #2) suggest that avoiding intentional or unintentional spraying of black liquor on the waterwall surface should reduce corrosion rates in these areas of the recovery boiler.

DISCUSSION:

Task I - Corrosive Environment in Boiler #2:

Introduction

The lower furnace of some recovery boilers is known to have areas with high and low corrosion rates. If the material of construction is the same in both areas, then the cause for different corrosion rates can be attributed to the environment that comes in contact with the water wall. There are three environmental parameters that can play a role (individually or in combination) in determining corrosion behavior in lower furnaces of recovery boilers: the gaseous environment that the waterwall material is exposed to, the local tube surface temperature, the presence and the chemical composition of the frozen smelt on the waterwalls.

Previous published work indicated that the recovery boiler gases mainly contain nitrogen, carbon dioxide, carbon monoxide, hydrogen, methane, and oxygen with very low concentrations of sulfur-bearing gases (like hydrogen sulfide, sulfur dioxide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide). However, those reports were based on analysis of gases taken from the bulk of recovery boiler. From the corrosion point of view, gas composition should be analyzed closest to the waterwall material in question. In this study, gas samples from the waterwall surface were analyzed using an online chromatograph.

Temperature effect on chemical reactions is generally significant. However, high temperature corrosion is usually controlled by the protective film or scale that develops on the metal surface and acts as a barrier for the corrosive furnace gases to directly come in contact with the metal surface. In the lower furnace of the recovery boiler, thin scale on the waterwall tubes consists mainly of iron sulfide. Thermal excursions are believed to occur in the lower furnace that can potentially damage the scale and can cause higher corrosion rates by introducing microcracks in the sulfide scale. This phenomenon makes thermal excursions a potential source for high corrosion.

The presence of smelt on the waterwall surface in the lower furnace of the boiler acts as an insulator and also shields the tube material from the gaseous environment. It was postulated that smelt composition might change in different areas of the boiler and affect the corrosion rate of tube material and, hence, produces areas with different corrosion rates.

Test Procedures

Monitoring the corrosive environment in Boiler #2 was done in a similar fashion to Boiler #1. This monitoring is divided into three tasks: furnace gas sampling, temperature monitoring of the waterwall membrane, and smelt collecting. The procedure for carrying out each task is published in the March 1999 Annual Program Review. There were two gas-sampling ports, vertically one foot apart, and four thermocouples in each area.

Two areas were selected based on the mill's annual ultrasonic tube thickness data. However, the mill has continued to make changes in their firing practices and air supply in recent years. Past corrosion behavior in the two areas must have been due to differences in the local environment. However, our results indicated that recent operational changes were found to have changed local corrosive environments in the two areas. Although in this report we distinguish areas by their historic waterwall corrosion behavior, but recent changes have significantly changed the corrosivity of local environments. Historically, higher corrosion rates were found in the middle of the front and back walls, whereas lower corrosion rates were found in the corners of the boiler.

Sampling ports were installed in Boiler #2 to monitor three environmental parameters. Those ports were installed in each selected area during shutdown according to the schematic shown in Figure 1.Two stainless steel gas-sampling ports were welded onto waterwall membrane to support the ceramic tubes that were inserted from the cold side of the boiler to sample the boiler gas. This design is air leak-free and was implemented successfully in Boiler #1. All sampling ports were designed so that they can be accessed from the cold side of the boiler. Gas samples were extracted and directly injected into the GC for immediate analysis. Gas samples were taken from one inch, one foot, and two feet away from the membrane and toward the center of the boiler. Gas samples were also taken from the waterwall surface web, as this is the environment that membrane material is exposed to. Samples from the waterwall surface are referred to as flush samples in this report.

Four web-embedded thermocouples were installed in each area, as is shown in Figure 1. The tip of each thermocouple was 0.25" from the fireside surface (0.75" from the cold side) of the membrane, and they were fully accessible from the cold side of the boiler. All eight thermocouples were calibrated in lab before using them in the mill, and they were connected to a data logger.

One smelt-sampling (collecting) port was installed in each area in similar fashion to gas-sampling ports. Smelt ports could be connected to the N_2-gas chamber that was equipped with a specially designed ceramic spatula to prevent oxidation of smelt. The chamber could be tightened on the port with the N_2 flowing and the spatula inserted and left for sometime to allow smelt to accumulate. Then the spatula was retrieved into a nitrogen-filled chamber. This chamber was

placed in a glove bag, filled with N_2 gas, and left to cool down. Once the temperature dropped to a manageable level, the chamber was disassembled and the smelt was stored in an air-tight container.

The effort in the mill was concentrated on collecting gas samples from flush and 1-inch depths to generate as much data as possible, as these locations are the most relevant to the corrosion of waterwall tubes. It must be noted that the gas analysis reported here is based on a dry gas mixture (without water vapors). One difference in Boiler #2's gas sampling from Boiler #1's gas sampling is that in Boiler #2 there were two gas sampling ports, upper (U) and lower (L), per area. This was done to see if there were any differences in gas concentrations within a particular corrosion area at different heights in the boiler. However, one of many similarities between the two boilers was that the high corrosion area in both boilers was in the middle of waterwall while the low corrosion area was close to the corner of the boiler.

Results

Analysis of chromatograms developed from Boiler #2 was done in a lab at IPST. The results of these analyses are summarized in Tables I & II.

As mentioned above, the gas analysis wasreported on a dry gas bases (i.e., excluding water vapor from the sample). This is one of the reasons why mass balance of each gas analysis does not add up to 100%.

A high corrosion area was found close to the black liquor gun, in the middle of the waterwalls. This area was significantly affected by the turbulent flow of gases in the recovery boiler. Flow of gases in the corners was less turbulent due to flow parameters and boiler configuration. The pattern of spraying black liquor in the recovery boiler was found to be of great importance in understanding the causes of corrosion areas in both recovery boilers. The concentration of gases at 2-foot depth was rich in N_2 and CO_2 in the high corrosion area and rich in H_2, CH_4, CO, and H_2S in the low corrosion area, as shown in Tables I and II. This might be due to thorough mixing of air in the 2-foot sample therefore causing N_2 and CO_2 to be higher. However, gases are relatively stagnant in the corner of the boiler, so gas samples are rich in gases that are produced locally due to heating and pyrolysis of black liquor.

From corrosion point of view, flush (and 1 inch) samples are the most significant for corrosion of waterwalls. A summary of average gas concentration in the two areas at flush position is given in Table III. The concentration of gases in flush samples was richin N_2 and CO_2 in the high corrosion area and rich in H_2, CH_4, and CO in the low corrosion area. From thermodynamic calculations, it is known that methyl mercaptan gives higher sulfur partial pressure than H_2S and COS. The question is whether this low level of methyl mercaptan is responsible for the difference in corrosion rate in a very complex gaseous mixture boiler #1 and #2.

If the corrosive gaseous environment is sulfidizing and the sulfur-bearing gases (e.g., H_2S, COS, and MM) are the only source of sulfur (assuming no interaction among gases), then there is no great difference in the partial pressure of sulfur in the two selected areas of Boiler #2. These results are summarized in Table IV. Temperature monitoring of the two areas was done by eight

thermocouples imbedded in the membrane at 0.75" from the cold side. Figure 1 is showing a typical temperature profile for the eight thermocouples during approximately one full day (23 hours). The profile is showing no significant difference between the two areas and no thermal excursions either. Hence, there is not a thermal differences between the two areas of interest and temperature does not play a role in producing the different corrosion rates. After a number of attempts, smelt samples could not be collected from Boiler #2. However, based on previous work, smelt is not expected to be different in the two areas in question.

Historic wall thickness data from annual inspections show that in the past two areas had different corrosion rates, but recent changes in firing practices as well as air supply has changed the local environment in these areas. The results indicate that the two areas were very similar in terms of gaseous and thermal environments. Based on these results, if operating conditions remain the same, we do not anticipate any significant differences in the corrosion rates in these areas in the future.

Conclusions

Based on our results from Boiler #1 and 2, the following conclusions can be drawn (Results from Boiler #1 were included in 1999 annual program review report):

1. Based on our results from Boiler #1 and Boiler #2, temperature differences or temperature fluctuations did not have a significant influence on the differences in the corrosion rates of waterwall tubes in the two selected areas in the selected boilers.

2. In Boiler #1, the smelt was not found on the waterwall surface in the selected areas at the liquor gun level; therefore, differences in smelt compositions should not affect corrosion in the selected areas. However, in Boiler # 2 there was evidence of a thin layer of smelt in both selected areas, but smelt samples could not be extracted through installed ports.

3. Analyses of recovery boiler gases have shown that the concentration of sulfur-bearing gases is significantly higher at the waterwall surface in areas with high corrosion than in the bulk gases or at the waterwall surface in areas with low corrosion.

4. Higher concentrations of sulfur-bearing gases in the high corrosion area in Boiler #1 were due to direct spraying of black liquor at the waterwalls in this area. Therefore, sulfur-bearing species were available in the local area to react with the waterwall surface causing higher rates of corrosion than in other areas of the waterwall.

5. Direct spraying of black liquor may also lead to localized scale damage through thermal shock and expose underlying metal to localized high concentrations of sulfur-bearing gases in the high corrosion region.

6. In Boiler #2, where the liquor is not intentionally sprayed on waterwalls, gaseous environments in the two selected boilers were very similar. Based on these results, one can predict that the waterwall corrosion rates will be low and very similar in the two selected areas of Boiler #2

7. Results from this study suggest that avoiding intentional or unintentional spraying of black liquor on the waterwall surface should reduce corrosion rates in these areas of the recovery boiler.

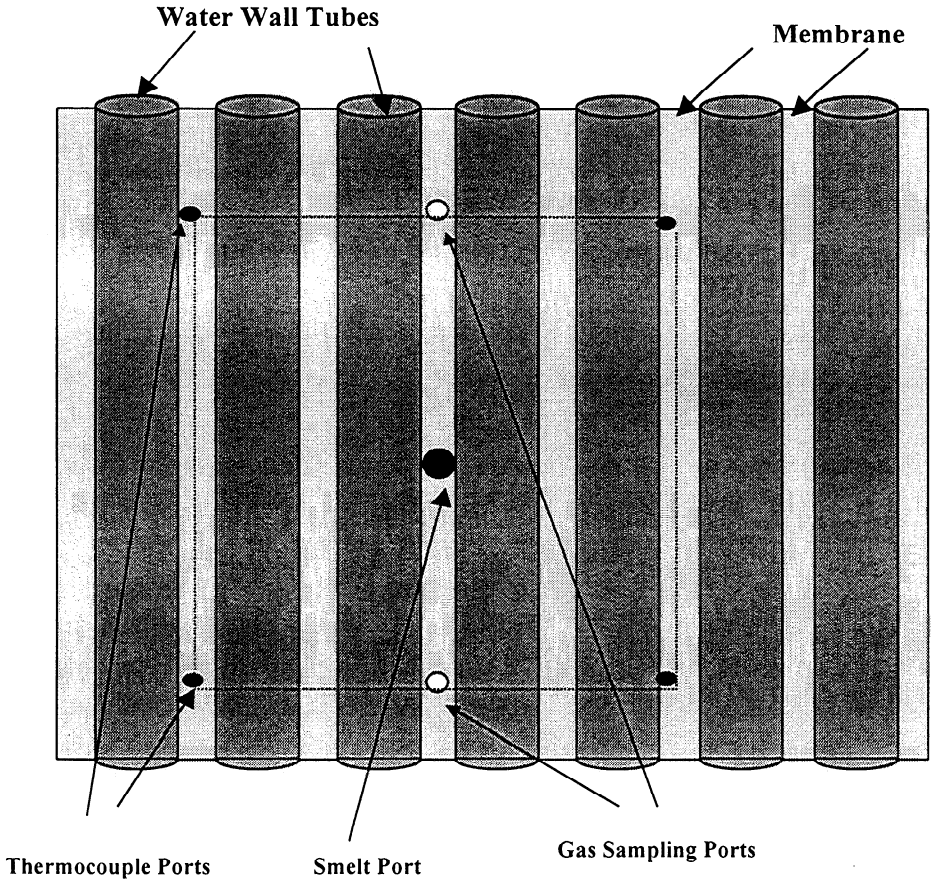

Figure 1. Schematic showing general layout of sampling ports for gas, temperature, and smelt installed in the high and low corrosion areas of recovery Boiler #2.

Task II - Alternative to On-Line Gas Sampling For Gas Characterization

Introduction

As one very important task for this project, we evaluated alternative ways to carry gas samples to the lab instead of taking a gas chromatograph to the mill. Although on-line gas chromatographs have performed very well in field, carrying gas analysis equipment to the mill and operating it there is expensive and and it limits our ability to analyze boiler gases to only those areas of the boiler where the bulky equipment can be placed in the mill. It would be very useful to find some means of shipping and storing recovery boiler gas samples for a certain period without significantly changing the gas composition. This would allow us to carry out corrosive environment monitoring in different parts of the boiler. With the present method, we can only monitor gases while in the mill and, therefore, we miss changes in the environment that may

result from changes in operating parameters at other times in a given boiler. With new storage methodology, mill personnel can be trained to take appropriate gas samples at or after such operational changes and ship them to the lab for analysis. Such samples can be extracted from any part of the boiler where proper sampling ports can be installed to avoid any sample contamination. We intend to continue this effort during future boiler monitoring.

Test Procedures and Results

Two types of gas-sampling containers were chosen for initial testing, a glass container equipped for gas sampling and a Tedlar bag, which is a special plastic bag claimed to be resistant to sulfur gases. Both containers were tested in this preliminary study where multiple recovery boiler gas samples were collected from Boiler #2, and were shipped to IPST for their analysis in lab. In the lab, gas samples were analyzed over different time periods. In our initial tests, glass containers were found to be superior to Tedlar bags for maintaining the gas composition intact. Glass bulbs were found to be capable of keeping the gas mixture under pressure and not allowing significant gas diffusion to change the gas composition. Furthermore, the septum or seal of the containers was found to be important as in the case of glass containers where the inlet was made of two layers of different plastics, a design that helps to control gas leaks. We have yet to determine if such a septum design in Tedlar bags will improve their performance. We also need to take more samples to determine whether the concentration of recovery gases can change with time due to gas reactions during storage.

Task III - Laboratory Tests on Carbon Steel Specimens in Recovery Boiler Gas Environments:

Introduction

Research task III is to determine corrosion rates in simulated recovery boiler environments and compare them with the reported corrosion rates from the mill records. Tests are being conducted in complex gaseous environment representing gases from high and low corrosion areas in Boiler #1 at two different temperatures for two weeks by using thermobalance. In one set of tests, water vapor will be added to the gaseous mixture to investigate its effect on corrosion rate of carbon steel in sulfidizing environment.

Test Procedures and Results

Carbon steel specimens were also tested in individual sulfur bearing gases in thermobalance to evaluate the effect of individual gas constituents on overall corrosion of waterwalls in kraft recovery boilers at high temperatures. Hydrogen sulfide and carbonyl sulfides were the first two gases tested in this project. They were chosen because they represent the major sulfur-bearing gases found in both boilers. These gases were tested at 320°C for 15 days, as shown in Figure 2. As indicated by Figure 2, corrosion behavior of carbon steel was similar for both gases. This correlates well with the free energy of dissociation for both gases releasing sulfur, which can further participate in sulfidation of iron in carbon steel, as shown below:

$2H_2S\,(g) = S_2\,(g) + 2H_2\,(g)$ $\quad\quad$ ΔG at 320°C = 28.88 kCal

$2COS\,(g) = S_2\,(g) + 2CO\,(g)$ $\quad\quad$ ΔG at 320°C = 21.28 kCal

Differences in Gibb's free energy for these two reactions is not very significant. Further tests in other sulfur-bearing gases may also be carried out individually in the future.

Second series of tests are underway where the carbon steel specimens (SA-210) are exposed to the recovery boiler gases (high corrosion and low corrosion areas in boiler #1). These tests are carried out in thermal balance. Required gases were mixed, using electronic flow-meters, to simulate boiler gas mixtures. Tests are expected to complete by June 2000 and the results will be reported to in next annual project review.

Table I. Average concentration of dry gases (wt. %) in samples taken from upper (U) and lower (L) ports in a high-corrosion area at different distances from the tube membrane.

Location/ Gas	Flush		1 in		1 ft		2 ft	
	U	L	U	L	U	L	U	L
H_2	0.3002	0.3996	0.2408	0.6329	0.0602	0.1710	0.0707	-
CO_2	29.2862	28.5140	36.9350	18.1710	36.9816	34.7390	36.1531	-
O_2	3.2966	3.7544	0.9362	5.1181	1.0484	0.7320	1.1663	-
N_2	56.7034	37.6240	63.6910	27.6050	76.1557	63.0460	82.4808	-
CH_4	2.5672	4.2649	1.9636	5.0307	0.8899	2.6100	0.4094	-
CO	13.3862	23.0960	8.4878	28.5310	3.5695	5.9160	2.2260	-
H_2S	0.4148	0.5141	0.1961	0.2624	0.0213	0.2220	0.0111	-
COS	0.0972	0.1930	0.0198	0.0742	0.0084	0.0133	0.0223	-
MM	0.0130	0.0300	0.0070	0.0040	0	0	0	-
DMS	0.0050	0.0050	0.0005	0.0004	0	0	0	-
CS_2	0.0006	0.0015	0	0.0004	0	0	0	-
DMDS	0.0014	0.0016	0.0014	0.0018	0	0.0022	0	-

Table II. Average concentration of dry gases (wt. %) in samples taken from upper (U) and lower (L) ports in a low-corrosion area at different distances from the tube membrane.

Location/ Gas	Flush		1 in		1 ft		2 ft	
	U	L	U	L	U	L	U	L
H_2	0.4799	0.6015	0.6949	0.6217	0.5311	-	0.7822	-
CO_2	22.2670	20.0360	19.1373	25.2140	31.1156	-	26.319	-
O_2	1.2907	4.1831	0.8792	0.3721	0.9713	-	1.0189	-
N_2	22.6660	29.2980	12.8844	21.5480	27.2889	-	18.032	-
CH_4	7.7601	8.5794	8.4297	5.2853	4.7548	-	7.2659	-
CO	30.2620	22.3050	29.2930	38.0940	23.7527	-	26.364	-
H_2S	0.3792	0.5341	0.5443	0.7774	0.5583	-	0.5221	-
COS	0.0954	0.1493	0.0064	0.2623	0.1541	-	0.1152	-
MM	0.0027	0.0041	0.0004	0.0170	0.0023	-	0.0085	-
DMS	0.0018	0.0050	0	0.0029	0.0019	-	0.0057	-
CS_2	0	0.0005	0	0.0004	0	-	0.0007	-
DMDS	0.0022	0.0041	0.0035	0.0017	0.0025	-	0.0039	-

Table III. Average concentration of dry gases (wt. %) in samples from high-corrosion area (H) and low-corrosion area (L) at flush position with the tube membrane.

Location/Gas	High	Low
H_2	0.3499	0.5407
CO_2	28.9000	21.152
O_2	3.5255	2.7369
N_2	47.1640	25.9820
CH_4	3.4160	8.1697
CO	18.2410	26.2830
H_2S	0.4644	0.4567
COS	0.1451	0.1224
MM	0.0212	0.0034
DMS	0.0047	0.0034
CS_2	0.0010	0.0003
DMDS	0.0015	0.0031

Table IV. Sulfur partial pressure from major sulfur-bearing gases at flush position with tube membrane, calculated from thermodynamic values at 260°C.

Location/ Gases	High Corrosion Area		Low Corrosion Area	
	%	P_{S2}	%	P_{S2}
H_2S	0.4644	2.08 E-6	0.4567	2.06E-06
COS	0.1451	7.69E-6	0.1224	6.86E-6
MM	0.0212	0.0176	0.0034	0.0052
Total		0.0176098		0.0052089

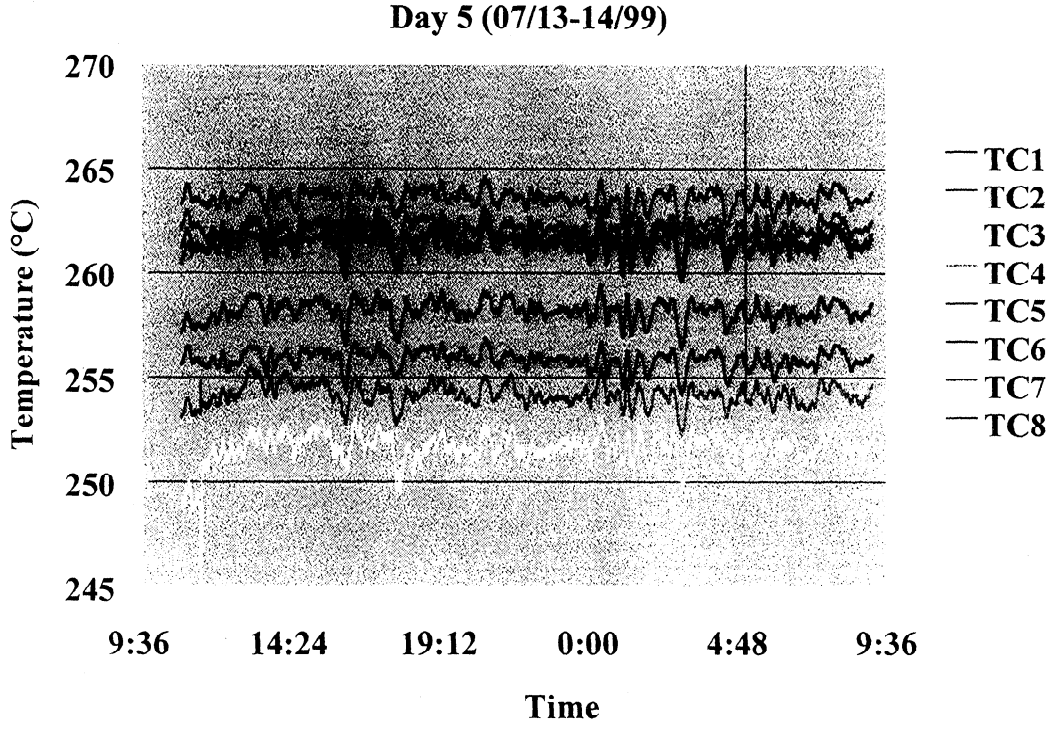

Figure 2. Temperature profile of waterwall in two corrosion areas using web-imbedded thermocouples, 0.25 inch from the fireside showed no significant difference in temperature between the two areas. Differences between different thermocouples are due to their installation and were constant.

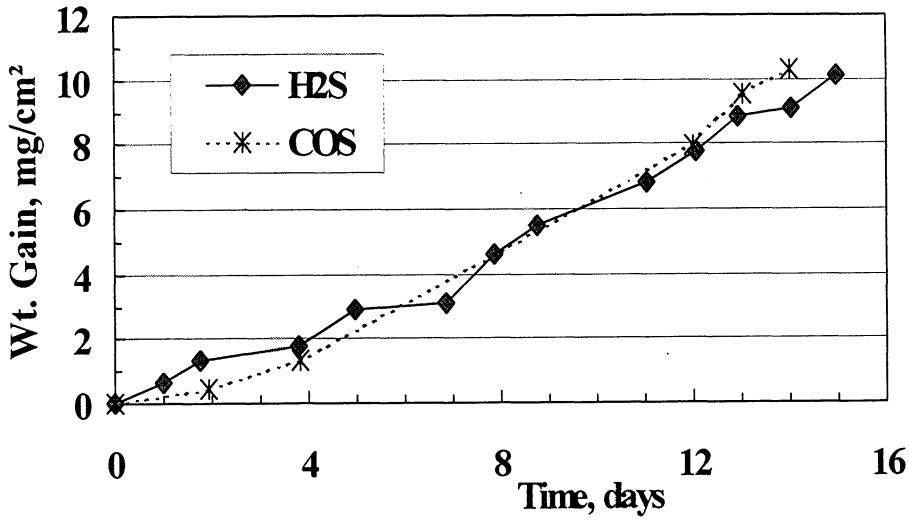

Figure 3. SA-210 carbon steel tested in one of the sulfur-bearing gases at 320°C in thermobalance.

DUES-FUNDED PROJECT SUMMARY

Project Title:	**CORROSION IN CLOSED CYCLE MILLS**
Project Code/Project Number:	**F019**
PAC:	**Corrosion Control**
Project Duration:	**Finished in July 1999**
Project Staff	
Principal Investigator:	**Preet Singh**
Co-Investigators:	**N/A**
Research Support Staff:	**Greg Fonder, Jamshad Mahmood**
PAC Subcommittee	**N/A**
FY 99-00 Budget:	**$0.00**
Allocated as Matching Funds:	**0%**
Time Allocation:	
Principal Investigator:	**0%**
Co-Investigators:	**N/A**
Research Support Staff:	**0%**
Supporting Research:	
Special Students:	**N/A**
External (Where matching is used):	**N/A**

RESEARCH LINE/ROADMAP:
Research Line #9 - Reduce lifetime costs of construction by 30% through innovative technologies

Research Line #7 - Develop forming technologies that use less water

PROJECT OBJECTIVES:
To identify key corrosion and materials-related issues that may impact the successful implementation of various closed mill scenarios and to provide support to maximize the potential of the new closed mill technologies.

PROJECT BACKGROUND:
The following effects are expected due to closure of white-water system:

1. An increase in temperature due to recirculation of warm water.
2. Changes in the chemical composition depending upon the papermaking process and the strategies applied to mill closure.
3. Changes in pH that depend upon the initial pH and chemical changes.
4. An accumulation of dissolved organic species like starch that may lead to increased microbial activity. This, in turn, can lead to microbial corrosion in the white-water system.

The above stated environmental changes can affect the corrosivity of white water. Corrosivity of closed white water will depend upon various process parameters and the design of mill closure. Effects on any particular equipment will depend upon the material used as well as on the environment that comes in contact with this material.

The main objective of this project was to study the effects of mill closure on corrosion of equipment in contact with white water.

BENEFITS TO INDUSTRY:
Prediction of materials behavior in closed white-water systems and therefore, in-time mitigation strategies for successful implementation of processes essential to reduce water consumption. Cost-effective material selection for closed white-water environments. Results from the corrosion fatigue tests on roll materials in closed white-water system will show if an increase in the overall concentration of chemicals in white water, or an increase in certain chemical species like Cl^- ion concentration has any effect on the crack growth rate or threshold stress intensity of duplex stainless steel.

STATUS OF GOALS FOR FY 1999-00:
- Coupon exposure tests for localized corrosion susceptibility in four different whitewaters representing acid and alkaline papermaking processes - by March 2000
- Complete fog chamber tests to simulate continuous mist areas in the paper mill by - December 2000
- Test pre-cracked compact tension specimens of VKA378 alloy in TAPPI-D, ten times concentrated TAPPI-D, and TAPPI-D with higher chlorides. Tests were completed by July 1999. A new project proposal was submitted to RAC for further work on corrosion fatigue of rolls.
- Report results to member companies through annual program review – March 2000

DELIVERABLES:
Relative ranking of materials in four simulated white water compositions representing different closed white-water scenarios. This will help mills make materials-related decisions in closed white water systems. All tests done by March 2000.

Corrosion fatigue behavior, crack growth rate vs stress-intensity relationships of commonly used roll materials in closed white waters. These will help in risk analysis and life prediction of rolls for safe operation. Work to investigate these effects on one roll material AKA 378, as recommended by PAC, is finished and results are included in this report.

SCHEDULE:

Task Descriptions	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
Complete one year long coupon exposure tests	----------	----------	----------	-------X	
Conduct fog chamber tests	-------	----------	------X		
Corrosion fatigue tests in three simulated closed white waters	----------	---------X			
Analyze data and write report		----	----------	X	

SUMMARY OF RESULTS:

This study was conducted to investigate the effects of increase in the chemical concentration of white water, due to mill closure, on the corrosion susceptibility of equipment and other metallic structures that may be exposed to this environment. Along with commonly used austenitic stainless steel grades 304L and 316L, five higher alloys were also tested to generate localized corrosion data for these candidate materials, which are resistant to white water systems. Tested materials included 317L, SAF 2205, SAF 2507, 254 SMO, and 654 SMO alloys.

Four different white water compositions were used in this study. TAPPI-D white water with pH of 4 and 9 were baseline solutions in this study, whereas solutions with ten times concentration represent closed white waters. Immersed coupon exposure tests for up to 360 days have shown that 304L is susceptible to localized corrosion attack, both pitting and crevice corrosion, in all tested white waters. There was an increase in the corrosion attack with ten times the increase in chemical concentration compared to the TAPPI-D white water. 316L specimens were also susceptible to localized attack in all tested white waters; however, the extent of attack was less in 316L specimens than for 304L specimens. Other tested alloys (i.e., 317L, SAF 2205, SAF 2507, 254 SMO, and 654 SMO) did not show any signs of localized or general corrosion attack in any of the tested white waters for up to 360 days of exposure. Clearly these materials show resistance to localized corrosion in closed white-water systems and, therefore, are candidates for such applications. However, their selection will depend upon other property requirements for the structural component, or availability, and relative costs.

Areas in the paper mill that are exposed to the white-water mist are of concern because chemical concentrations in these areas can build up and cause accelerated corrosion of structural components of the mill. Tests were carried out in a fog chamber to simulate such environments. However, time for drying was not allowed in these tests, and the samples were continuously exposed to the mist environments. Alloys tested included Carbon steel, 304L, 316L, 317L, SAF 2205, SAF 2507, 254 SMO, and 654 SMO alloys. Tests were carried out in TAPPI-D white water with pH 4. Results from up to six-month exposure have shown that carbon steel is severely attacked in this environment. Structural components like support beams and machine frame are

generally made out of carbon steel. Such components need to be protected with protective paints or other protection strategies to ensure structural integrity of such components. Results have also shown that the rest of the tested alloys, including 304L specimens, did not shown any signs of localized or general corrosion in continuous-mist environments.

Changes in corrosion fatigue behavior of suction rolls due to changes in the environmental conditions in closed mills present a safety concern in paper mills. Threshold stress, below which a known crack does not grow, decreases with an increase in concentration of aggressive ions like chloride ions in the system. Whereas, the crack growth rate at any given stress intensity increases with similar changes. As a preliminary study, one duplex stainless steel roll material, VKA378, was tested in different environments representing open and closed mill scenarios. Results indicated that the threshold stress intensity did not vary much for the tested environments. However, the crack growth rate was higher in white waters with higher chloride concentrations. Solution with ten times the concentration of TAPPI-D white water did not show any increase in crack growth rate in VKA 378 specimens compared to the baseline TAPPI-D white water.

SUMMARY OF KEY CONCLUSIONS:

1. Results from this study show that 304L is not suitable for white water-systems because this material is susceptible to localized corrosion in tested white waters.
2. 316 stainless steel is relatively more resistant to localized corrosion than the 304L steel but is not totally immune to localized corrosion attack in most of the white waters. Higher alloys including 317L, 2205, 2507, 254 SMO, and 654 SMO are very resistant to localized attack in the tested white waters.
3. Results from corrosion fatigue tests on VKA378 duplex stainless steel, used as suction roll material, indicate that the threshold stress intensity did not vary much for the tested environments.
4. Crack growth rate was higher in white waters with higher chloride concentrations.

DISCUSSION:

Task I - Immersion Tests with Crevice Coupons

Introduction

The main objective of this project was to study the effects of mill closure on the corrosion of equipment in contact with white water. Changes in the corrosion behavior of any particular equipment will depend upon the material of construction as well as on the environment that comes in contact with this material.

Closed white-water systems are expected to have higher temperatures, increased concentrations of dissolved inorganic and organic chemicals, changes in pH, and increased microbial activity due to increases in dissolved organics. However, the extent of these changes will depend upon the system closure design and the initial values of these parameters before mill closure. These environmental changes may also affect the corrosivity of white water.

It is not practical during this project to verify the material behavior in every possible closed white-water scenario, so an experimental program was designed to answer the following concerns:

- How will different materials perform in concentrated white-water solutions, assuming that the concentration of major inorganic constituents of white water will increase in a closed mill? This situation can also arise in the open white waters in the areas where concentrations can build up due to alternate immersion in or evaporation of water.
- How will different materials behave in fog/mist areas of paper machines in closed white water systems?
- What will be the effect of increased chemical composition on fatigue behavior of roll materials, especially the effects on threshold stress intensities and crack growth rates?

Results from different tests carried out to investigate these effects have been described in results section starting from page 22.

Test Procedures:

Seven different materials: 654 SMO, 254 SMO, 2205, 2507, 304L, 316L, and 317L were used in this study. One side of each coupon was polished to a 1000-grit finish, whereas the other side of the coupon had a 120-grit finish. Individual racks were assembled with one coupon of each material in each rack, as was described in the 1999 annual program review report. Every coupon had a serrated crevice washer on each surface. Precautions were taken to eliminate any galvanic contact between the bolt holding the crevice washer and the coupon or within different coupons. To study the effects of cold work on corrosion susceptibility of the tested materials, three small cold-worked areas were also stamped on each side of the coupon. Coupons were tested for 15 days one month, two months, three months, six months, and one year.

Twenty-four individual racks, similar to the one shown in Figure 4, were prepared for a given temperature (160°F). The volume of the solution in each test container was more than 25 ml/inch^2 of the exposed coupons, as recommended by the ASTM G48-97 standard practice. Test solutions were refreshed every day for the first week. Thereafter, solutions were refreshed every three days for the next two weeks, every week for the next sixteen weeks and bi-weekly for the last thirty-three weeks. The pH 9.0 and pH 4.0 test solutions were maintained for test purposes by adding NaOH or HCl, respectively.

Table V shows the test matrix of different white-water compositions being used for various tests. The white-water compositions were chosen with the objective of determining the concentration limits that can be safely handled by a given material.

Table V. Simulated White-Water Solution Compositions

Environment	pH	Cl^- ppm	SO_4^{-2} ppm	$S_2O_3^{-2}$ ppm
Base Line – pH4	4.0	200	500	50
Strong Solution-10 – pH4	4.0	2000	5000	500
Base Line – pH9	9.0	200	500	50
Strong Solution-10 – pH9	9.0	2000	5000	500

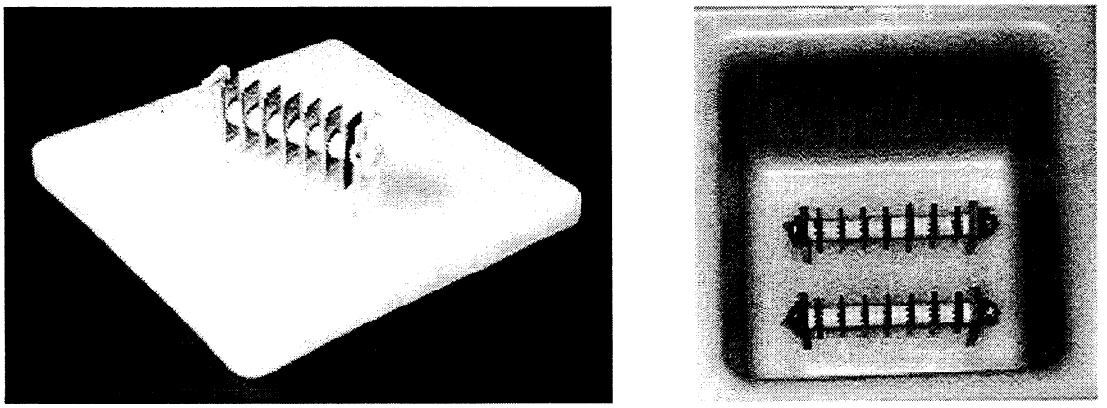

Figure 4. Pictures of a) coupon racks and b) containers used to expose them in a given environment used in this study.

Results

Chemical changes in white water during testing

Chemical analysis was performed after different time periods to quantify the change in the composition of the white water changed with time. Chemical analysis was performed on the fresh white water solution, solution used for coupons exposure, and the solution kept in the water bath but not exposed to test coupons. Chemical analysis has shown that there was no measurable change in the composition of white-waters at exposure temperature over a two-week period. However, ICP analysis has indicated that there were corrosion products in the exposed solutions. In high-pH, (9.0) simulated white-water, precipitated corrosion products were seen at the bottom of the container. Solution was collected from the top and the bottom of this container, and analysis clearly indicated that the bulk of the solution did not contain significant soluble metals, whereas the bottom sample for pH-9 solutions showed high concentrations of metal. Concentrations were found to be higher in the concentrated solution than in the baseline TAPPI-D white waters. These precipitates were insoluble hydroxides of iron, nickel and chromium and were only found under 304L specimen. They started to appear after about two days of exposure. Other specimens did not show any visible signs of corrosion on their surfaces in the first two weeks of exposure.

Crevice corrosion

Tables VI to XI show results from coupons with serrated washers exposed to different white waters at 160°F for different time periods up to one year. It was found that 304L material showed crevice attack after about 15 days in all of the tested white waters. The effect of chemical concentration on the probability of crevice attack was more pronounced for pH 9 solutions where more concentrated white water led to a higher probability of attack. However, in pH 4 solutions, the crevice attack was more severe and the probability of attack was very high even in the baseline low concentration white water.

316L specimens also showed occasional crevice attack; however, the probability of attack was very low compared to 304L specimens. Rough surfaces always had more susceptibility to crevice attack than smooth.

Except for the 304L and 316L material, no other material, including 317L, 2205, 2507, 254 SMO, and 654 SMO, showed any signs of crevice attack in all of the tested environments. These materials are definite candidates in closed white water systems, although their selection would also depend upon other properties and cost considerations.

Pitting corrosion

Tables XII through XVII show susceptibility of seven tested materials to pitting on general surfaces during up to one year of exposure in four different white waters, as listed in Table V. In general, pitting tendencies were similar to the crevice susceptibility of these materials in different environments. 304L specimens showed pitting attack after 15 days of exposure in all tested solutions. 316L did not show pitting for pH 4 baseline solution or in both alkaline solutions. However, in strong pH 4 solution, 316L specimens showed general pitting attack.. Pitting attack was more severe on rough surfaces and edges, which was due to the fact that inclusions intersecting these surfaces were attacked to initiate a pit. 316L data were not very consistent over different time periods, but clearly 316L was susceptible to pitting attack in all white waters, even though the susceptibility was less than the 304L specimens. The other five tested materials including 317L, 2205, 2507, 254 SMO, and 654 SMO did not show any signs of pitting attack on general surfaces or edges.

Conclusions

Based on coupon exposure test results it can be concluded that 304L is not a suitable material in most white-water applications. With mill closure, the susceptibility of 304L to localized corrosion attack is expected to be worse than for the open system, although our results indicate that even mills with open white water are not immune from this attack if they use 304L stainless steel.

316 stainless steel is relatively more resistant than the 304L steel to localized attack but is not totally immune to localized corrosion attack in most white waters.

Higher alloys including 317L, 2205, 2507, 254 SMO, and 654 SMO are very resistant to localized attack in the tested white waters. These alloys are expected to perform well in most closed white-water applications, unless the corrosivity of a particular white water is more than the tested solutions.

Table VI. Results from crevice coupons exposed to different white-water environments for fifteen days.

Material	Test Solution	pH	Temp °F	Crevice Attack on Rough Surface	Crevice Attack on Smooth Surface
304-L	Baseline pH 4	4.0	160	10/12	0/12
316-L	Baseline pH 4	4.0	160	0/12	0/12
317-L	Baseline pH 4	4.0	160	0/12	0/12
2205	Baseline pH 4	4.0	160	0/12	0/12
254-SMO	Baseline pH 4	4.0	160	0/12	0/12
654-SMO	Baseline pH 4	4.0	160	0/12	0/12
2507	Baseline pH 4	4.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 4	4.0	160	7/12	9/12
316-L	Strong Sol.-10 pH 4	4.0	160	3/12	3/12
317-L	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2205	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2507	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
304-L	Baseline pH 9	9.0	160	2/12	4/12
316-L	Baseline pH 9	9.0	160	0/12	0/12
317-L	Baseline pH 9	9.0	160	0/12	0/12
2205	Baseline pH 9	9.0	160	1/12	0/12
254-SMO	Baseline pH 9	9.0	160	0/12	0/12
654-SMO	Baseline pH 9	9.0	160	0/12	0/12
2507	Baseline pH 9	9.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 9	9.0	160	11/12	2/12
316-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
317-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2205	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2507	Strong Sol.-10 pH 9	9.0	160	0/12	0/12

Serrated crevice washer had 12 sections. 0/12 means that none of the sections had crevice corrosion attack, whereas 6/12 means that six sections had corrosion while the other six sections were not attacked.

Table VII. Results from crevice coupons exposed to different white-water environments for thirty days.

Material	Test Solution	pH	Temp °F	Crevice Attack on Rough Surface	Crevice Attack on Smooth Surface
304-L	Baseline pH 4	4.0	160	11/12	0/12
316-L	Baseline pH 4	4.0	160	0/12	0/12
317-L	Baseline pH 4	4.0	160	0/12	0/12
2205	Baseline pH 4	4.0	160	0/12	0/12
254-SMO	Baseline pH 4	4.0	160	0/12	0/12
654-SMO	Baseline pH 4	4.0	160	0/12	0/12
2507	Baseline pH 4	4.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 4	4.0	160	8/12	1/12
316-L	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
317-L	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2205	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2507	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
304-L	Baseline pH 9	9.0	160	8/12	0/12
316-L	Baseline pH 9	9.0	160	0/12	0/12
317-L	Baseline pH 9	9.0	160	0/12	0/12
2205	Baseline pH 9	9.0	160	0/12	0/12
254-SMO	Baseline pH 9	9.0	160	0/12	0/12
654-SMO	Baseline pH 9	9.0	160	0/12	0/12
2507	Baseline pH 9	9.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 9	9.0	160	10/12	2/12
316-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
317-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2205	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2507	Strong Sol.-10 pH 9	9.0	160	0/12	0/12

Serrated crevice washer had 12 sections. 0/12 means that none of the sections had crevice corrosion attack, whereas 6/12 means that six sections had corrosion while the other six sections were not attacked.

Table VIII. Results from crevice coupons exposed to different white-water environments for sixty days.

Material	Test Solution	pH	Temp °F	Crevice Attack on Rough Surface	Crevice Attack on Smooth Surface
304-L	Baseline pH 4	4.0	160	6/12	0/12
316-L	Baseline pH 4	4.0	160	0/12	0/12
317-L	Baseline pH 4	4.0	160	0/12	0/12
2205	Baseline pH 4	4.0	160	0/12	0/12
254-SMO	Baseline pH 4	4.0	160	0/12	0/12
654-SMO	Baseline pH 4	4.0	160	0/12	0/12
2507	Baseline pH 4	4.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 4	4.0	160	7/12	6/12
316-L	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
317-L	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2205	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2507	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
304-L	Baseline pH 9	9.0	160	1/12	0/12
316-L	Baseline pH 9	9.0	160	1/12	0/12
317-L	Baseline pH 9	9.0	160	0/12	0/12
2205	Baseline pH 9	9.0	160	0/12	0/12
254-SMO	Baseline pH 9	9.0	160	0/12	0/12
654-SMO	Baseline pH 9	9.0	160	0/12	0/12
2507	Baseline pH 9	9.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 9	9.0	160	12/12	0/12
316-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
317-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2205	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2507	Strong Sol.-10 pH 9	9.0	160	0/12	0/12

Serrated crevice washer had 12 sections. 0/12 means that none of the sections had crevice corrosion attack, whereas 6/12 means that six sections had corrosion while the other six sections were not attacked.

Table IX. Results from crevice coupons exposed to different white-water environments for ninety days.

Material	Test Solution	pH	Temp °F	Crevice Attack on Rough Surface	Crevice Attack on Smooth Surface
304-L	Baseline pH 4	4.0	160	12/12	0/12
316-L	Baseline pH 4	4.0	160	0/12	0/12
317-L	Baseline pH 4	4.0	160	0/12	0/12
2205	Baseline pH 4	4.0	160	0/12	0/12
254-SMO	Baseline pH 4	4.0	160	0/12	0/12
654-SMO	Baseline pH 4	4.0	160	0/12	0/12
2507	Baseline pH 4	4.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 4	4.0	160	12/12	1/12
316-L	Strong Sol.-10 pH 4	4.0	160	2/12	0/12
317-L	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2205	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2507	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
304-L	Baseline pH 9	9.0	160	0/12	0/12
316-L	Baseline pH 9	9.0	160	0/12	0/12
317-L	Baseline pH 9	9.0	160	0/12	0/12
2205	Baseline pH 9	9.0	160	0/12	0/12
254-SMO	Baseline pH 9	9.0	160	0/12	0/12
654-SMO	Baseline pH 9	9.0	160	0/12	0/12
2507	Baseline pH 9	9.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 9	9.0	160	8/12	2/12
316-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
317-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2205	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2507	Strong Sol.-10 pH 9	9.0	160	0/12	0/12

Serrated crevice washer had 12 sections. 0/12 means that none of the sections had crevice corrosion attack, whereas 6/12 means that six sections had corrosion while the other six sections were not attacked.

Table X. Results from crevice coupons exposed to different white-water environments for hundred-and-eighty days.

Material	Test Solution	pH	Temp °F	Crevice Attack on Rough Surface	Crevice Attack on Smooth Surface
304-L	Baseline pH 4	4.0	160	12/12	0/12
316-L	Baseline pH 4	4.0	160	1/12	0/12
317-L	Baseline pH 4	4.0	160	0/12	0/12
2205	Baseline pH 4	4.0	160	0/12	0/12
254-SMO	Baseline pH 4	4.0	160	0/12	0/12
654-SMO	Baseline pH 4	4.0	160	0/12	0/12
2507	Baseline pH 4	4.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 4	4.0	160	5/12	2/12
316-L	Strong Sol.-10 pH 4	4.0	160	4/12	0/12
317-L	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2205	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2507	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
304-L	Baseline pH 9	9.0	160	0/12	0/12
316-L	Baseline pH 9	9.0	160	0/12	0/12
317-L	Baseline pH 9	9.0	160	0/12	0/12
2205	Baseline pH 9	9.0	160	0/12	0/12
254-SMO	Baseline pH 9	9.0	160	0/12	0/12
654-SMO	Baseline pH 9	9.0	160	0/12	0/12
2507	Baseline pH 9	9.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 9	9.0	160	11/12	2/12
316-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
317-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2205	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2507	Strong Sol.-10 pH 9	9.0	160	0/12	0/12

Serrated crevice washer had 12 sections. 0/12 means that none of the sections had crevice corrosion attack, whereas 6/12 means that six sections had corrosion while the other six sections were not attacked.

Table XI. Results from crevice coupons exposed to different white-water environments for three-hundred-and-sixty days.

Material	Test Solution	pH	Temp °F	Crevice Attack on Rough Surface	Crevice Attack on Smooth Surface
304-L	Baseline pH 4	4.0	160	12/12	0/12
316-L	Baseline pH 4	4.0	160	1/12	0/12
317-L	Baseline pH 4	4.0	160	0/12	0/12
2205	Baseline pH 4	4.0	160	0/12	0/12
254-SMO	Baseline pH 4	4.0	160	0/12	0/12
654-SMO	Baseline pH 4	4.0	160	0/12	0/12
2507	Baseline pH 4	4.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 4	4.0	160	10/12	2/12
316-L	Strong Sol.-10 pH 4	4.0	160	3/12	0/12
317-L	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2205	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
2507	Strong Sol.-10 pH 4	4.0	160	0/12	0/12
304-L	Baseline pH 9	9.0	160	2/12	0/12
316-L	Baseline pH 9	9.0	160	0/12	0/12
317-L	Baseline pH 9	9.0	160	0/12	0/12
2205	Baseline pH 9	9.0	160	0/12	0/12
254-SMO	Baseline pH 9	9.0	160	0/12	0/12
654-SMO	Baseline pH 9	9.0	160	0/12	0/12
2507	Baseline pH 9	9.0	160	0/12	0/12
304-L	Strong Sol.-10 pH 9	9.0	160	9/12	2/12
316-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
317-L	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2205	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
254-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
654-SMO	Strong Sol.-10 pH 9	9.0	160	0/12	0/12
2507	Strong Sol.-10 pH 9	9.0	160	0/12	0/12

Serrated crevice washer had 12 sections. 0/12 means that none of the sections had crevice corrosion attack, whereas 6/12 means that six sections had corrosion while the other six sections were not attacked.

Table XII. Results showing pitting corrosion susceptibility of coupons exposed to different white-water environments for fifteen days.

Material	Test Solution	pH	Temp °F	Pits on Rough Surface	Pits on Smooth Surface	Pitting on Edges
304-L	Baseline pH 4	4.0	160	HP	FP	HP
316-L	Baseline pH 4	4.0	160	NP	NP	NP
317-L	Baseline pH 4	4.0	160	NP	NP	NP
2205	Baseline pH 4	4.0	160	NP	NP	NP
254-SMO	Baseline pH 4	4.0	160	NP	NP	NP
654-SMO	Baseline pH 4	4.0	160	NP	NP	NP
2507	Baseline pH 4	4.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 4	4.0	160	HP	FP	HP
316-L	Strong Sol.-10 pH 4	4.0	160	FP	NP	FP
317-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
304-L	Baseline pH 9	9.0	160	P	NP	FP
316-L	Baseline pH 9	9.0	160	NP	NP	NP
317-L	Baseline pH 9	9.0	160	NP	NP	NP
2205	Baseline pH 9	9.0	160	NP	NP	NP
254-SMO	Baseline pH 9	9.0	160	NP	NP	NP
654-SMO	Baseline pH 9	9.0	160	NP	NP	NP
2507	Baseline pH 9	9.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 9	9.0	160	HP	FP	HP
316-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
317-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP

FP = Few Pits (less than 10 pits on surface); Pitting = Pitting Attack (more than 10 & less than 30 pits on surface); HP = Heavy Pitting (More than 30 pits on surface); NP = No Pitting Attack

Table XIII. Results showing pitting corrosion susceptibility of coupons exposed to different white-water environments for thirty days.

Material	Test Solution	pH	Temp °F	Pits on Rough Surface	Pits on Smooth Surface	Pitting on Edges
304-L	Baseline pH 4	4.0	160	P	FP	HP
316-L	Baseline pH 4	4.0	160	NP	NP	NP
317-L	Baseline pH 4	4.0	160	NP	NP	NP
2205	Baseline pH 4	4.0	160	NP	NP	NP
254-SMO	Baseline pH 4	4.0	160	NP	NP	NP
654-SMO	Baseline pH 4	4.0	160	NP	NP	NP
2507	Baseline pH 4	4.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 4	4.0	160	FP	FP	HP
316-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	FP
317-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
304-L	Baseline pH 9	9.0	160	H P	NP	FP
316-L	Baseline pH 9	9.0	160	NP	NP	NP
317-L	Baseline pH 9	9.0	160	NP	NP	NP
2205	Baseline pH 9	9.0	160	NP	NP	NP
254-SMO	Baseline pH 9	9.0	160	NP	NP	NP
654-SMO	Baseline pH 9	9.0	160	NP	NP	NP
2507	Baseline pH 9	9.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 9	9.0	160	HP	NP	HP
316-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
317-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP

FP = Few Pits (less than 10 pits on surface); Pitting = Pitting Attack (more than 10 & less than 30 pits on surface); HP = Heavy Pitting (More than 30 pits on surface); NP = No Pitting Attack

Table XIV. Results showing pitting corrosion susceptibility of coupons exposed to different white-water environments for sixty days.

Material	Test Solution	pH	Temp °F	Pits on Rough Surface	Pits on Smooth Surface	Pitting on Edges
304-L	Baseline pH 4	4.0	160	FP	FP	P
316-L	Baseline pH 4	4.0	160	FP	NP	NP
317-L	Baseline pH 4	4.0	160	NP	NP	NP
2205	Baseline pH 4	4.0	160	NP	NP	NP
254-SMO	Baseline pH 4	4.0	160	NP	NP	NP
654-SMO	Baseline pH 4	4.0	160	NP	NP	NP
2507	Baseline pH 4	4.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 4	4.0	160	P	NP	HP
316-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
317-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
304-L	Baseline pH 9	9.0	160	FP	NP	FP
316-L	Baseline pH 9	9.0	160	FP	NP	NP
317-L	Baseline pH 9	9.0	160	NP	NP	NP
2205	Baseline pH 9	9.0	160	NP	NP	NP
254-SMO	Baseline pH 9	9.0	160	NP	NP	NP
654-SMO	Baseline pH 9	9.0	160	NP	NP	NP
2507	Baseline pH 9	9.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 9	9.0	160	HP	NP	P
316-L	Strong Sol.-10 pH 9	9.0	160	FP	NP	FP
317-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP

FP = Few Pits (less than 10 pits on surface); Pitting = Pitting Attack (more than 10 & less than 30 pits on surface); HP = Heavy Pitting (More than 30 pits on surface); NP = No Pitting Attack

Table XV. Results showing pitting corrosion susceptibility of coupons exposed to different white-water environments for ninety days.

Material	Test Solution	pH	Temp °F	Pits on Rough Surface	Pits on Smooth Surface	Pitting on Edges
304-L	Baseline pH 4	4.0	160	HP	NP	P
316-L	Baseline pH 4	4.0	160	NP	NP	NP
317-L	Baseline pH 4	4.0	160	NP	NP	NP
2205	Baseline pH 4	4.0	160	NP	NP	NP
254-SMO	Baseline pH 4	4.0	160	NP	NP	NP
654-SMO	Baseline pH 4	4.0	160	NP	NP	NP
2507	Baseline pH 4	4.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 4	4.0	160	HP	FP	HP
316-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	FP
317-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
304-L	Baseline pH 9	9.0	160	FP	NP	FP
316-L	Baseline pH 9	9.0	160	NP	NP	NP
317-L	Baseline pH 9	9.0	160	NP	NP	NP
2205	Baseline pH 9	9.0	160	NP	NP	NP
254-SMO	Baseline pH 9	9.0	160	NP	NP	NP
654-SMO	Baseline pH 9	9.0	160	NP	NP	NP
2507	Baseline pH 9	9.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 9	9.0	160	P	FP	HP
316-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
317-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP

FP = Few Pits (less than 10 pits on surface); Pitting = Pitting Attack (more than 10 & less than 30 pits on surface); HP = Heavy Pitting (More than 30 pits on surface); NP = No Pitting Attack

Table XVI. Results showing pitting corrosion susceptibility of coupons exposed to different white-water environments for hundred-and-eighty days.

Material	Test Solution	pH	Temp °F	Pits on Rough Surface	Pits on Smooth Surface	Pitting on Edges
304-L	Baseline pH 4	4.0	160	HP	FP	HP
316-L	Baseline pH 4	4.0	160	NP	NP	NP
317-L	Baseline pH 4	4.0	160	NP	NP	NP
2205	Baseline pH 4	4.0	160	NP	NP	NP
254-SMO	Baseline pH 4	4.0	160	NP	NP	NP
654-SMO	Baseline pH 4	4.0	160	NP	NP	NP
2507	Baseline pH 4	4.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 4	4.0	160	P	P	HP
316-L	Strong Sol.-10 pH 4	4.0	160	FP	NP	FP
317-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
304-L	Baseline pH 9	9.0	160	P	NP	P
316-L	Baseline pH 9	9.0	160	NP	NP	NP
317-L	Baseline pH 9	9.0	160	NP	NP	NP
2205	Baseline pH 9	9.0	160	NP	NP	NP
254-SMO	Baseline pH 9	9.0	160	NP	NP	NP
654-SMO	Baseline pH 9	9.0	160	NP	NP	NP
2507	Baseline pH 9	9.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 9	9.0	160	HP	FP	P
316-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
317-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP

FP = Few Pits (less than 10 pits on surface); Pitting = Pitting Attack (more than 10 & less than 30 pits on surface); HP = Heavy Pitting (More than 30 pits on surface); NP = No Pitting Attack

Table XVII. Results showing pitting corrosion susceptibility of coupons exposed to different white-water environments for three-hundred and-sixty days.

Material	Test Solution	pH	Temp °F	Pits on Rough Surface	Pits on Smooth Surface	Pitting on Edges
304-L	Baseline pH 4	4.0	160	HP	FP	HP
316-L	Baseline pH 4	4.0	160	NP	NP	NP
317-L	Baseline pH 4	4.0	160	NP	NP	NP
2205	Baseline pH 4	4.0	160	NP	NP	NP
254-SMO	Baseline pH 4	4.0	160	NP	NP	NP
654-SMO	Baseline pH 4	4.0	160	NP	NP	NP
2507	Baseline pH 4	4.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 4	4.0	160	HP	P	HP
316-L	Strong Sol.-10 pH 4	4.0	160	FP	NP	FP
317-L	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 4	4.0	160	NP	NP	NP
304-L	Baseline pH 9	9.0	160	P	NP	HP
316-L	Baseline pH 9	9.0	160	NP	NP	NP
317-L	Baseline pH 9	9.0	160	NP	NP	NP
2205	Baseline pH 9	9.0	160	NP	NP	NP
254-SMO	Baseline pH 9	9.0	160	NP	NP	NP
654-SMO	Baseline pH 9	9.0	160	NP	NP	NP
2507	Baseline pH 9	9.0	160	NP	NP	NP
304-L	Strong Sol.-10 pH 9	9.0	160	HP	FP	HP
316-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
317-L	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2205	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
254-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
654-SMO	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP
2507	Strong Sol.-10 pH 9	9.0	160	NP	NP	NP

FP = Few Pits (less than 10 pits on surface); Pitting = Pitting Attack (more than 10 & less than 30 pits on surface); HP = Heavy Pitting (More than 30 pits on surface); NP = No Pitting Attack

Conclusions

1. Results from this study show that 304L is not suitable for white water-systems because this material is susceptible to localized corrosion in tested white waters.
2. 316 stainless steel is more resistant to localized corrosion than the 304L steel but is not totally immune to localized corrosion attack in most of the white waters.
3. Higher alloys including 317L, 2205, 2507, 254 SMO, and 654 SMO are very resistant to localized attack in the tested white waters.

Task II - Salt Spray Tests for Mist/Fog Areas

Introduction

Certain areas of the paper machine are exposed to a continuous fine spray/mist of white water. The composition of this environment is expected to change with mill closure. The corrosion susceptibility of metals in a spray/mist environment can differ significantly from metals submerged in a similar environment. This study was initiated to characterize the corrosion behavior of various materials exposed to simulated white water fine spray/mist conditions in the spray booth.

Test Procedure

The salt spray cabinet is a deep, temperature-controlled chest, as shown in Figure 5, equipped with a spray tower that makes a fine mist of the salt solution. The spray droplets are directed so that they fall in a uniform pattern onto metal specimens that are suspended by insulated wires throughout the cabinet. Graduated cylinders are placed at different locations in the cabinet, at the level of the coupons, to ensure that all specimens are exposed to the same volume of mist. All spray/mist coming from the tower is fresh white-water solution. The used solution falls to the bottom of the booth where it collects in a layer several inches deep before it is drained away. This layer helps maintain a constant temperature and humidity in the cabinet.

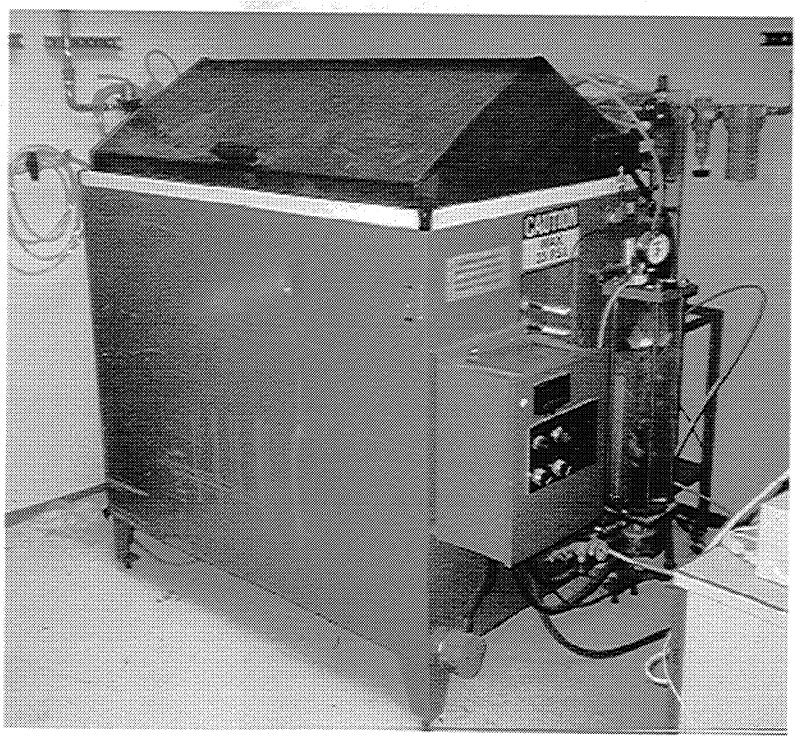

Figure 5. Spray cabinet used to perform salt spray tests

The test coupons used for these tests were made from eight materials: carbon steel, 304L, 316L, 317L, SAF 2205, SAF 2507, 254 SMO, and 654 SMO. A typical coupon used in this study is shown in Figure 6.

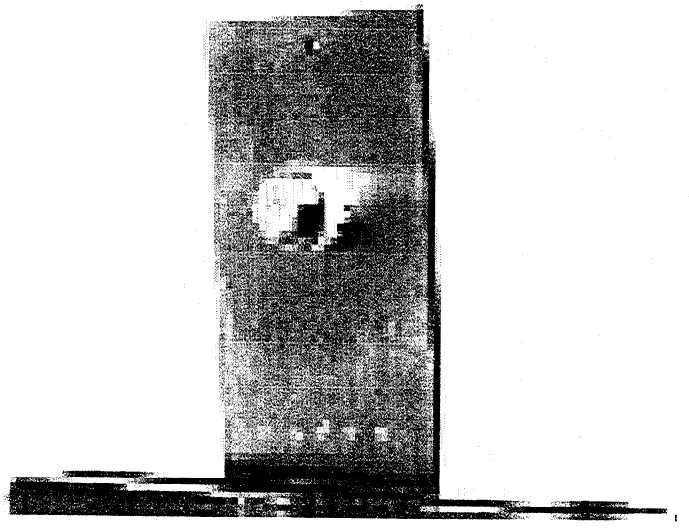

Figure 6. Coupon with crevice washers and cold-work spots

All coupons of a given material were cut from the same metal sheet to avoid any heat variation in the tested coupons. Cold-worked edges developed by sheet-cutting operations were removed from the coupons by milling 1/8 inch of materials from all edges. Two holes were drilled in each coupon; a small hole for the mounting wire to pass through and a larger hole to be used in conjunction with crevice washers. Each coupon was then polished to a 1700-grit finish on one side, while the other was left in the as-received condition. Five small cold-worked areas were stamped on the polished side to study the effect of cold-working on the corrosion susceptibility of the material.

The salt spray tests were performed in accordance with ASTM B-117. The procedure was modified in that a simulated white-water solution (TAPPI "D") was used in place of the salt solution described in the ASTM procedure. The coupons were thoroughly degreased in acetone prior to placement in the spray cabinet. Crevice washers were attached to the coupons in accordance with ASTM G48-97. Each coupon was placed in the spray cabinet by suspending it from a plastic support using an insulated wire. The coupons were placed in the cabinet so that the they were below the level of the spray tower. Then they were arranged to prevent contact therefore removing the unwanted complications of galvanic corrosion.

The initial plans for these tests were to expose the selected materials to four different environments; however, because of the termination of the project, only one environment was used. The target environment and the actual environment are given in Table XVIII. The coupons were exposed for time periods of 15, 30, 90, and 180 days. Multiple coupons were used for each exposure.

Table XVIII. Salt Spray Test Parameters

	Temperature	Flow Rate	SO_4^{2-}	$S_2O_3^{2-}$	Cl^-	pH
Nominal	95°F	0.2 gal/hr	500 ppm	50 ppm	200 ppm	4.0
Mixing Tank	N/A	N/A	432	47	184	4.05
Reservoir	N/A	0.2 gal/hr	412	43	178	4.17
Spray Booth	95°F	0.2 gal/hr	495	14	199	5.6

Results and conclusions

In these tests, samples were not allowed to intermittently dry and concentrations to built up on sample surface. These tests represent the areas of paper machine where metallic structures are exposed to the white-water mist continuously. These tests show that continuous white-water mist/fog environment is not corrosive to the stainless steels. Even 304L stainless steel samples did not show any signs of localized or general corrosion in up to six-month exposure. However, carbon steel samples showed active corrosion in this environment. Figure 7 shows the appearance of a carbon steel coupon after 90 days whereas Figure 8 shows a graph of the weight loss vs. time for carbon-steel for times up to 180 days. Corrosion of carbon steel increases with time. Corrosion scale on the carbon steel was loose and therefore does not seem to provide any barrier for corrosive environment to reach the metal surface. Therefore, carbon steel components

like beams and other structures need to be protected in this environment by using barrier coatings like paint or "stainless steel wallpaper".

Composition of fog droplets was analyzed by placing a beaker in the chamber and collecting condensed white-water. Table XVIII shows that the white-water composition in the mixing tank is very similar to the spray booth composition. However, pH of the collected sample was 5.6 compared to pH 4.0 for the mixing tank. This difference in pH might be due to long time needed to collect a sufficient amount of white-water sample in a beaker in the fog chamber for analysis.

Figure 7. Carbon steel coupon after 90 days exposure to TAPPI-D mist

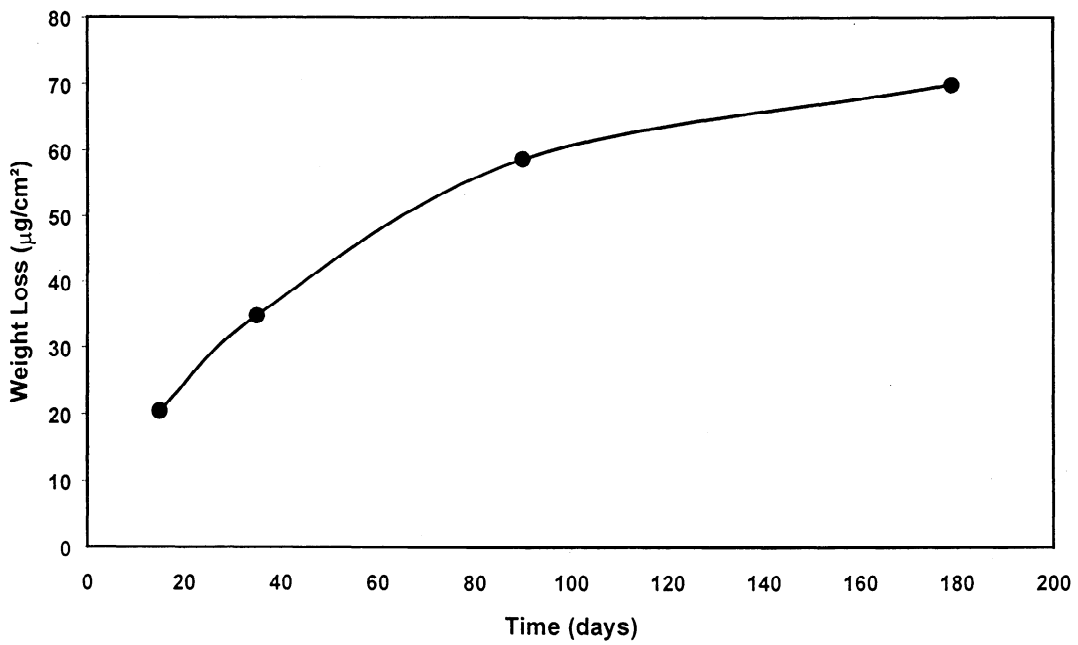

Figure 8. Weight loss of carbon steel coupon vs. time in TAPPI-D white-water mist

Task III - Fatigue Crack Growth Studies in Simulated White Waters

Introduction

Changes in corrosion fatigue behavior of suction rolls due to changes in the environmental conditions in closed mills are a safety concern in paper mills. Threshold stress, below which a known crack does not grow, decreases with an increase in aggressive ion concentration, like chloride ions in the system. Whereas, the crack growth rate at any given stress intensity increases with similar changes. The objective of this task was to study the corrosion fatigue behavior of a common suction roll material, VKA 378, in simulated white water. The crack threshold and crack growth rate were measured as a function of chloride concentration with all other components remaining the same and as a function of increasing concentration of all components of the simulated white water.

Test Procedures

Compact tension specimens were machined out of VKA 378 according to the ASTM E-647 procedure. The specimens were polished to a 1200-grit finish. The polishing was needed to avoid any effect of surface roughness on crack propagation as well as to easily monitor crack tip for growth rate measurements using a cathetometer. The specimen was then mounted on an MTS hydraulic testing machine, shown in Figure 9, for pre-cracking in air. The stress intensity, K, which the specimen was cracked with, was determined from previous experience at IPST. A value lower than that expected was initially applied. If no cracking occurred after 120,000 cycles, the stress intensity was increased by 1 $MPa \cdot m^{1/2}$. The ratio of the maximum tensile load to the minimum tensile, R, was chosen to be 0.5, the same as the value for the actual testing. The crack was allowed to grow to a length of several millimeters in accordance with ASTM test procedures. This study required the use of five specimens, and all were pre-cracked at the start of the testing. The specimens were removed from the MTS machine, thoroughly cleaned and degreased and stored in a desicator to be used for further testing.

The actual tests were conducted in a series of environments that were meant to simulate the increasingly concentrated white water the suction rolls on a paper machine would experience as mill closure progressed from less closed to a more closed condition. The environments used for these tests are given in Table XIX.

Table XIX - Fatigue Test Matrix

Environment	Temp °C	pH	Cl^- ppm	SO_4^{-2} ppm	$S_2O_3^{-2}$ ppm
Air	RT	-	-	-	-
Baseline TAPPI-D	50	4.0	200	500	50
10X TAPPI-D	50	4.0	2000	5000	500
TAPPI-D + 5Cl⁻	50	4.0	1000	500	50
TAPPI-D + 25Cl⁻	50	4.0	5000	500	50

All tests used VKA 378 as the specimen material, were of the rising K type, and were performed at a frequency of 25 Hz with R = 0.5.

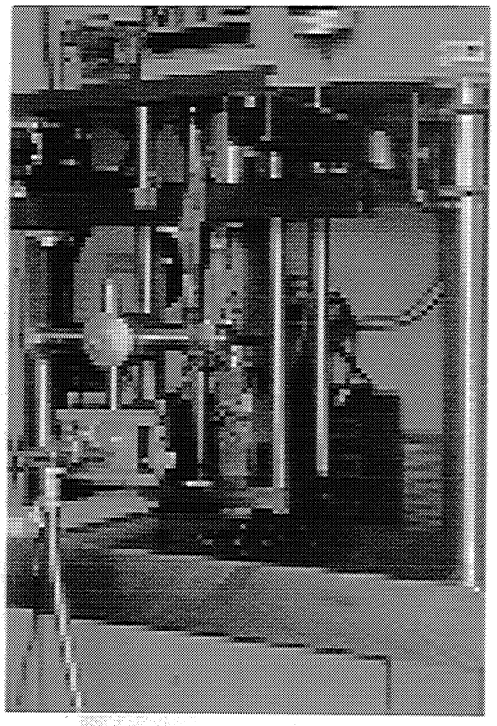

Figure 9. Testing apparatus for fatigue tests

Results

The initial test was conducted in air to get a baseline for the performance of the material. The results are shown in Figures 10 and 11. The first figure shows a curve typical of fatigue crack growth. The second shows the same values plotted as a log-log plot. The results of the remaining tests are shown in Figures 12-16. Micrographs in Figures 17 and 18 show fatigue crack path at different areas of the specimen, representing different applied stress intensities. The fatigue crack path does not discriminate between the two phases of this duplex stainless steel nor does it favor interface between these phases.

Figures 19 to 22 show the results of all the tests on one log-log plot and best-fit line for each set of data. A comparison of best-fit data for different environments gives a better idea of the effect of the various changes in the environment. Results from these tests have indicated that the threshold stress intensity for VKA378 duplex stainless steel does not vary much for the tested environments. However, the crack growth rate was higher in white waters with higher chloride concentrations. A solution with ten times the concentration of TAPPI-D white water did not show any increase in crack growth rate in VKA 378 specimens compared to the baseline TAPPI-D white water. This can also be attributed to the fact that in the ten-times solution, the ratio of chloride to sulfate remained the same as in the baseline solution, whereas in the high chloride

solution this ratio was higher. Further testing is required to answer some of the key questions regarding the effects of individual ions and the effects at even higher concentrations of ions in closed white waters on corrosion fatigue behavior of different roll materials.

Conclusions

- The changes in environment had little effect on the threshold stress intensity of VKA 378 material in tested white waters
- The crack growth rate increased for all environments over that in air at a given ΔK
- The addition of Cl^- to TAPPI D increased the crack growth rate at a given ΔK
- Increasing all components of the simulated white-water environment by the same ratio had no effect on crack growth rate or threshold stress intensity for crack growth.

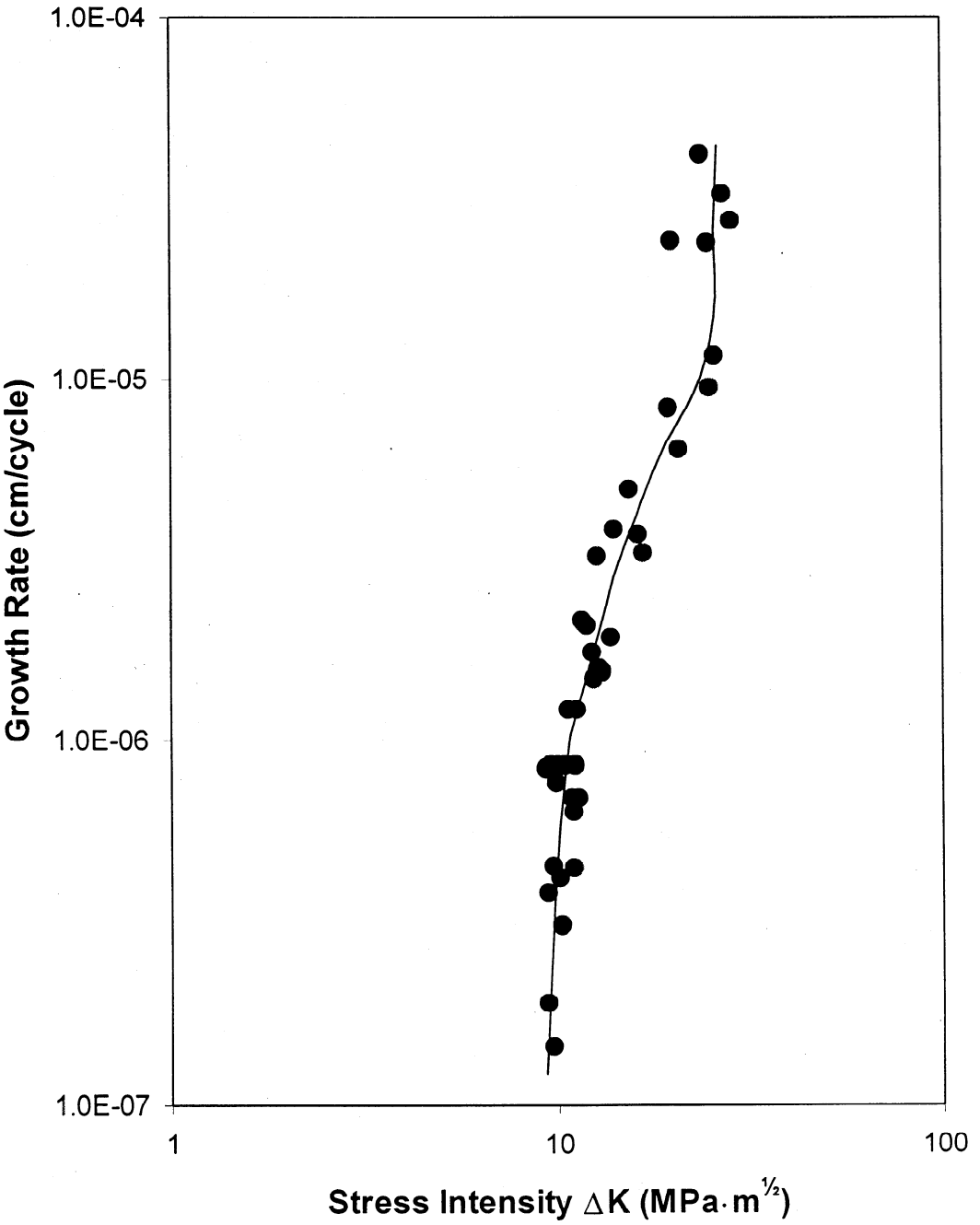

Figure 10. Fatigue crack growth for VKA 378 duplex stainless steel as a function of stress I intensity difference in air.

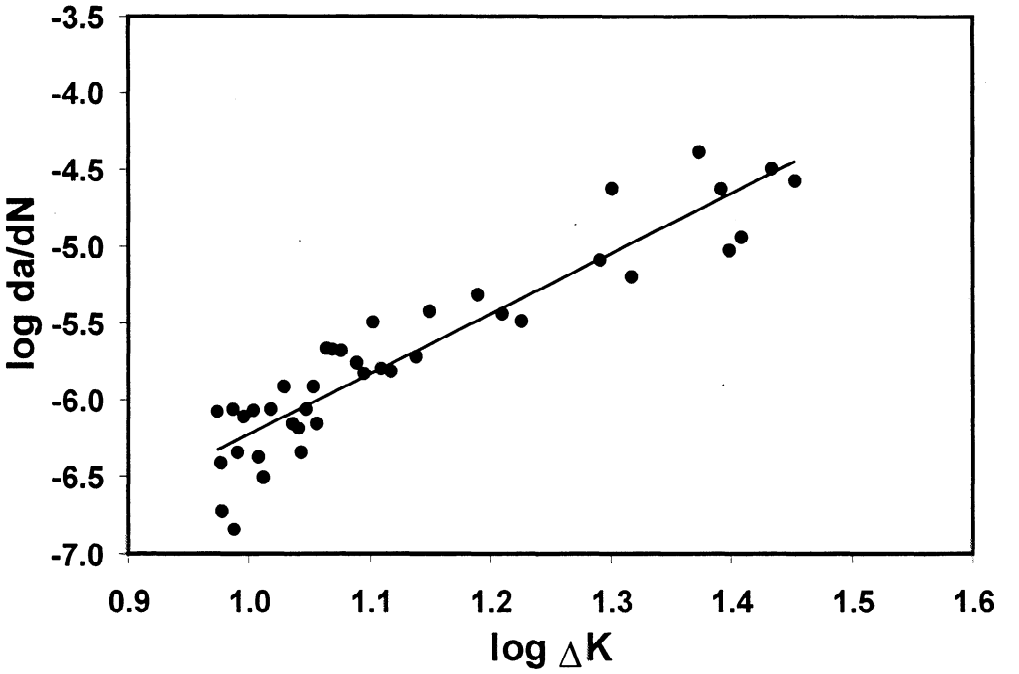

Figure 11. Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference in air.

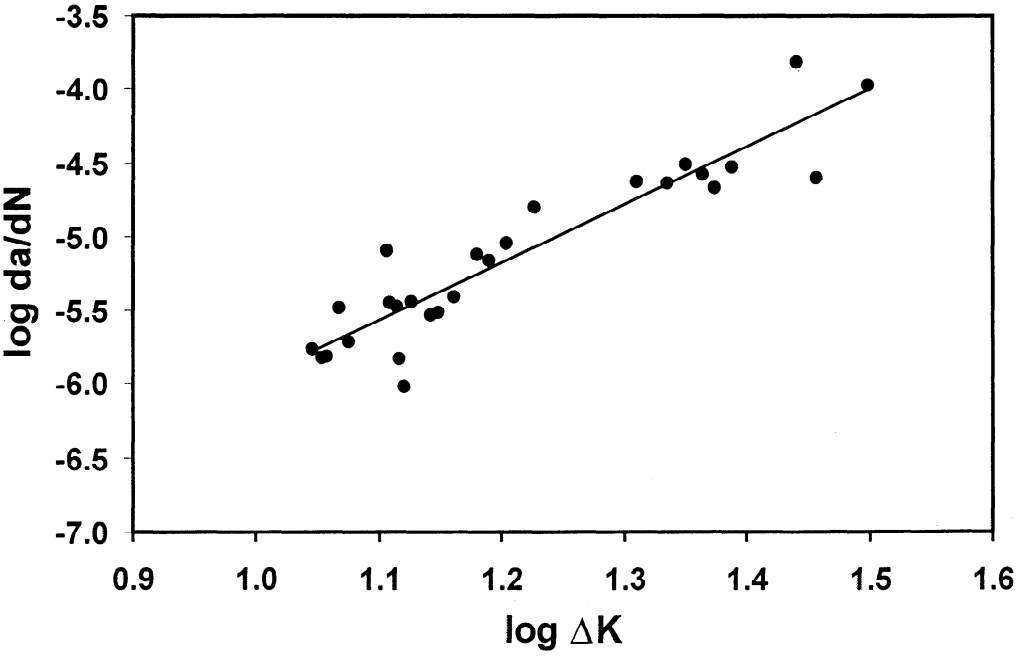

Figure 12. Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference in TAPPI-D white-water.

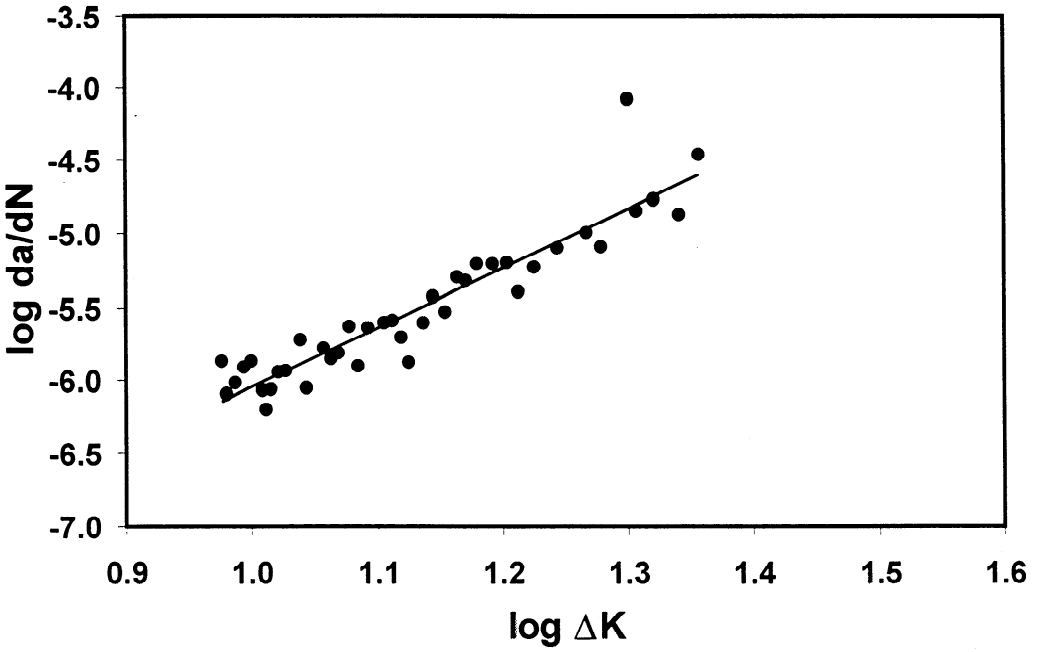

Figure 13. Fatigue crack growth VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference in 10X TAPPI-D white water.

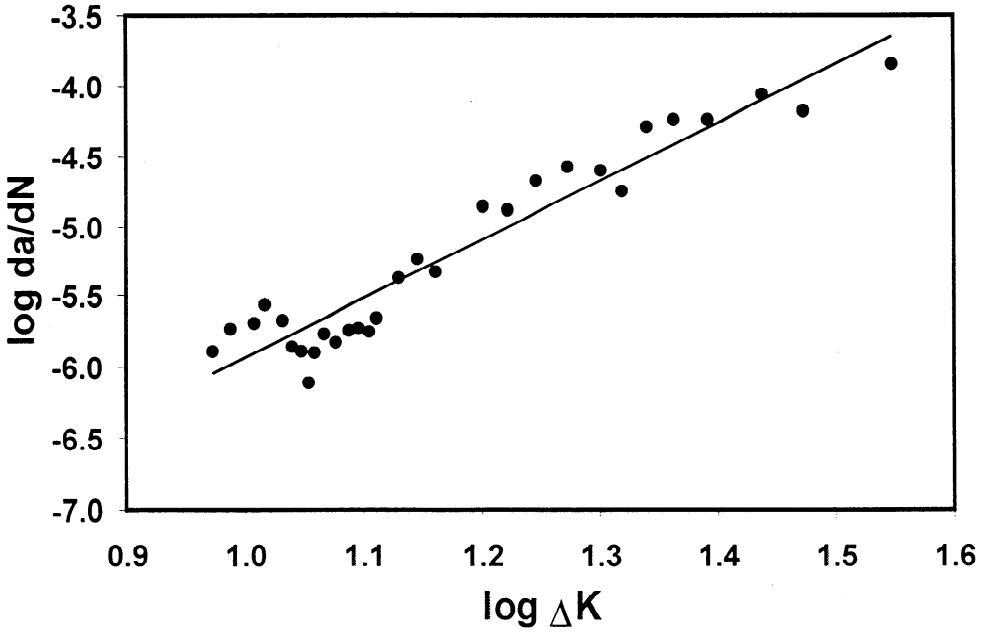

Figure 14. Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference in TAPPI-D + 5Cl^- white water.

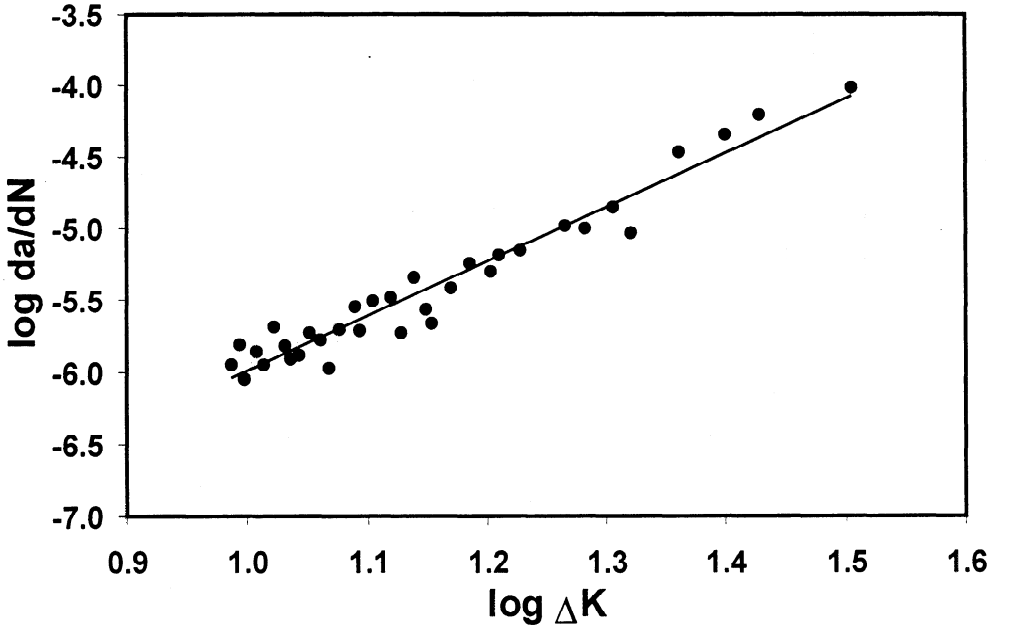

Figure 15. Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference in TAPPI-D + 25Cl⁻ white-water.

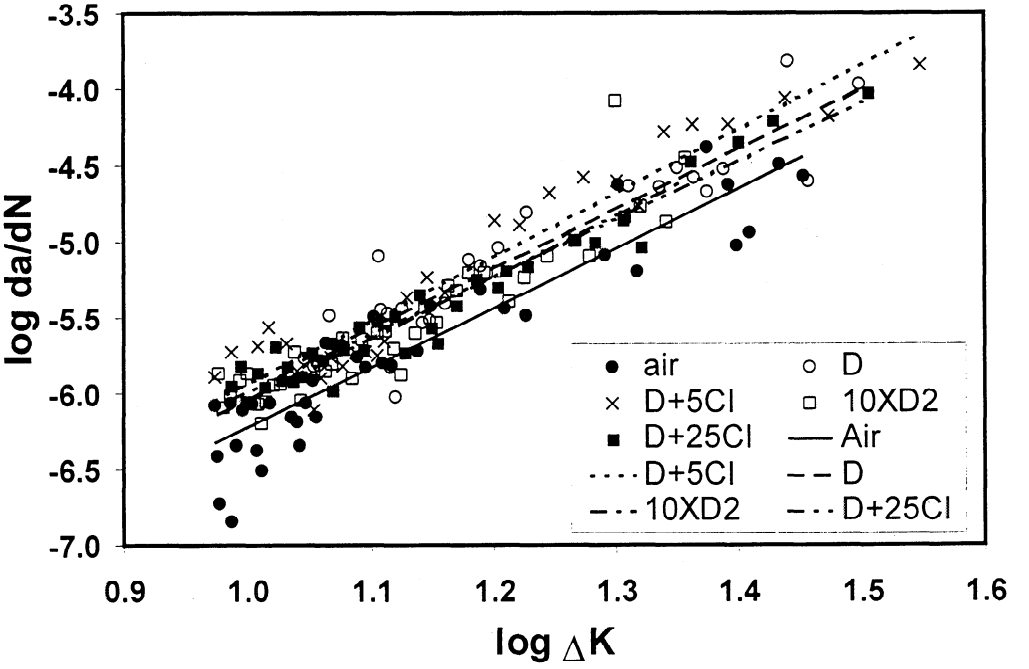

Figure 16. Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference in all tested environments.

Figure 17. Fatigue crack path near middle of a VKA 378 CT-specimen tested in TAPPI-D + 5Cl⁻. This crack does not seem to favor any particular phase or interface in this duplex alloy.

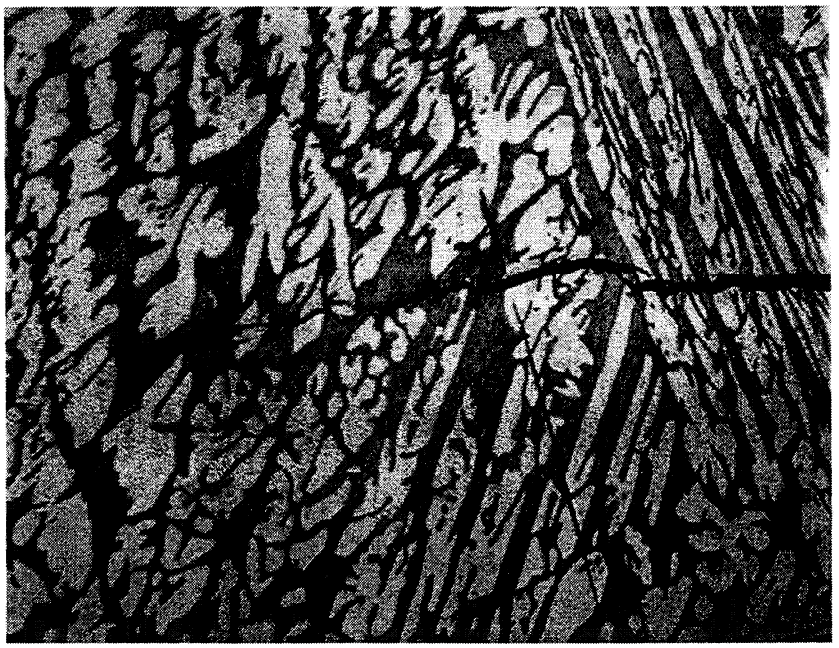

Figure 18. Fatigue crack path near tip of the crack for a VKA 378 CT-specimen tested in TAPPI-D + 5Cl⁻. Fatigue crack does not seem to favor any particular phase or interface in this duplex alloy.

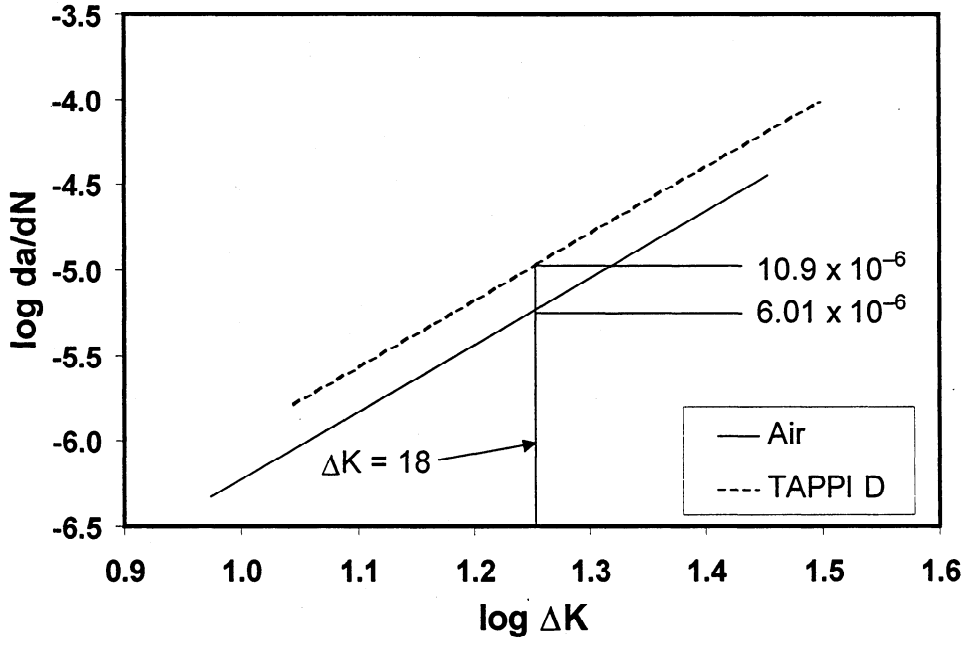

Figure 19. Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference showing trends for Air and TAPPI-D white-water.

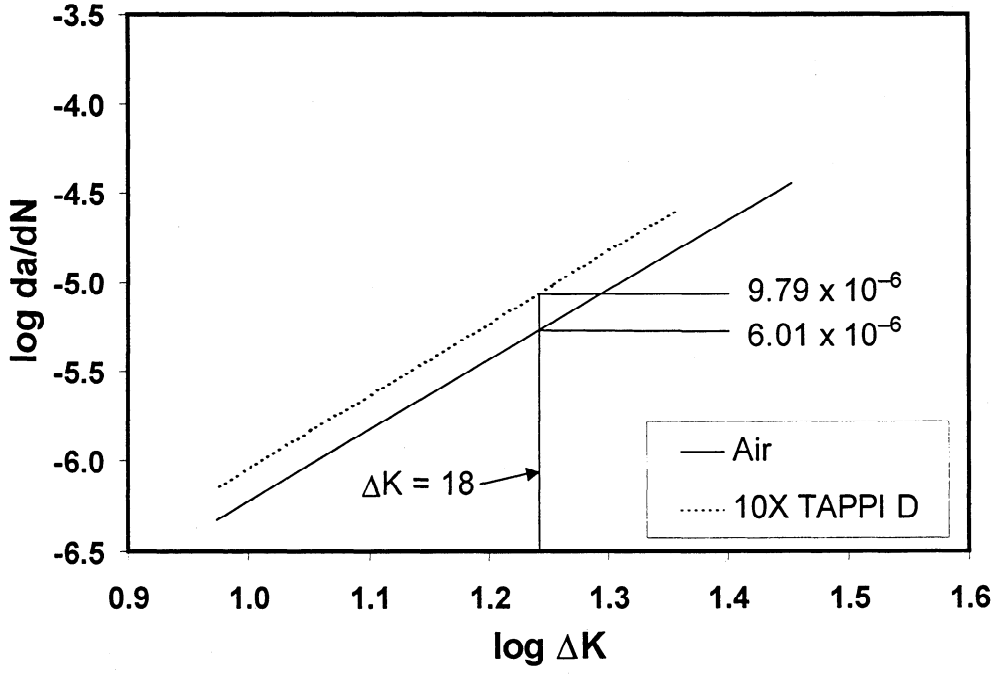

Figure 20. Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference showing trends for Air vs. 10X TAPPI-D white water

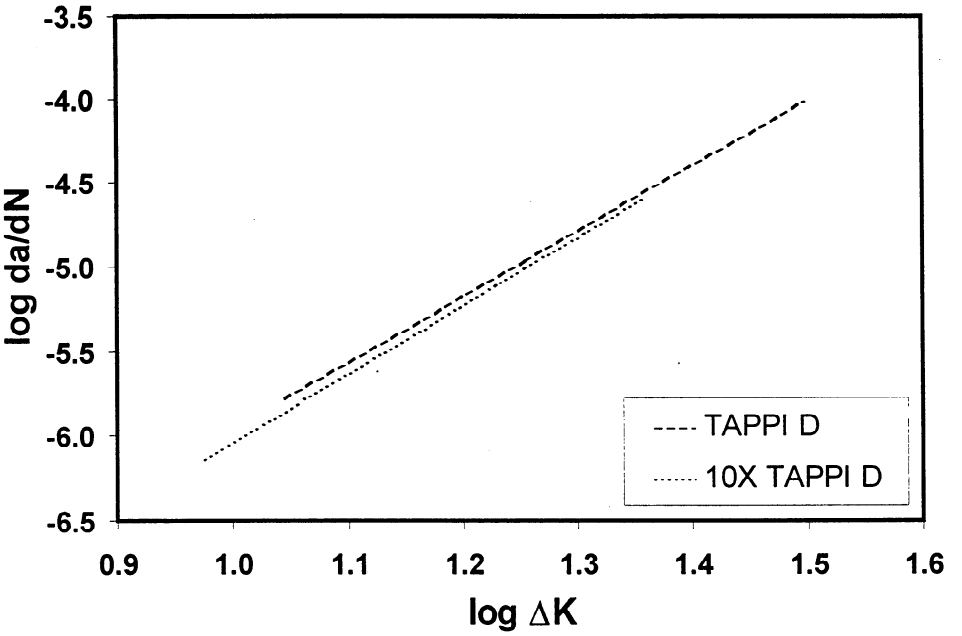

Figure 21 Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference showing trends for TAPPI-D vs. 10X TAPPI-D white waters.

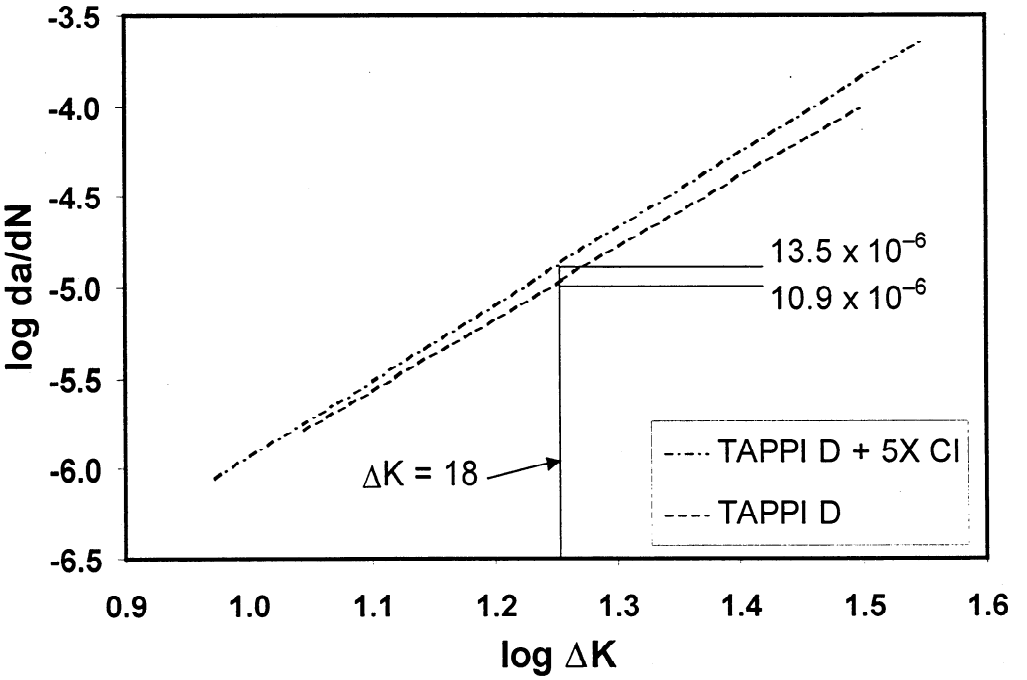

Figure 22. Fatigue crack growth for VKA 378 stainless steel in terms of log crack growth per cycle vs log stress intensity difference showing trends for TAPPI-D vs. TAPPI-D + $5Cl^-$ white waters.

DUES-FUNDED PROJECT SUMMARY

Project Title:	**Mechanisms and Prevention of Stress-Assisted Waterside Corrosion in Recovery Boilers**
Project Number:	**F036**
PAC:	**Corrosion Control**
Project Staff	
Principal Investigator:	**Preet Singh**
Co-Investigators:	**Greg Fonder**
Research Support Staff:	**Jamshad Mahmood**
PAC Subcommittee	**N/A**
FY 99-00 Budget:	**$89,342**
Allocated as Matching Funds:	**0%**
Time Allocation:	
Principal Investigator:	**19%**
Co-Investigators:	**60%**
Research Support Staff:	**10%**
Supporting Research:	
Special Students:	**N/A**
External (Where Matching Is Used):	**N/A**

RESEARCH LINE/ROADMAP:
Research Line #8 - Improve operations and control of current recovery boilers

Research Line #9 - Reduce lifetime costs of construction by 30% through innovative technologies

PROJECT OBJECTIVES:
Remedial measures related to water treatment, chemical cleaning, operating practice and improved materials of construction to mitigate SAC in recovery boiler waterwalls. This project will provide industry-specific support to a major 2020 research project at Oak Ridge National Laboratories. The project will build on previous research in the utility industry to study the mechanism of stress-assisted corrosion in recovery boilers and its relationship to attachment weld design.

PROJECT BACKGROUND:

Corrosion or cracks in the boiler tubes can lead to water leaks in the boiler that can potentially lead to boiler explosion. One of the insidious corrosion mechanisms responsible for boiler corrosion is from the waterside and is called stress-assisted corrosion cracking (SAC). SAC of waterwall tubes poses safety and operation-related problems to kraft recovery boilers. Each year this forces many mills to replace significant portions of waterwall panels at a cost of millions of dollars for each boiler. It is almost impossible to quantitate the value of eliminating such cracks, but at least one major smelt-water explosion in 1991 was reported to be due to a combination of stress-assisted waterside corrosion and external corrosion. SAC is also referred to as corrosion fatigue or stress cracking by some in the pulp and paper industry and other industries with power boilers. Generally these types of failures are associated with attachment welds where structures are welded on to waterwall tubes. If not detected during non-destructive inspections earlier, the failure of tubes results in pinhole leaks on the cold side or casing side of the tube, near attachment welds. SAC cracking is experienced throughout the boilers. This type of failure is very difficult to detect during a normal shutdown of the boiler because the cracks start from the waterside and are not visible from outside. Also, due to limitations of detection techniques, the cracks are particularly difficult to detect in the corners and areas that are not easily accessible. SAC problem is becoming more prominent as boilers age or as awareness of this problem forces operators to look for this mode of failure in their boilers.

This type of failure is also found in other power boilers in the pulp and paper industry and other power industry. Systematic work was carried out under an EPRI project to understand the root cause of welded tube attachment cracking. However, boiler design, operating parameters, and other practices like shutdown procedures that are different in different industries may affect waterwall side cracking of boiler tubes.

One major difference between the kraft recovery boiler and the utility boiler is that we can not have water leaking in kraft boilers due to explosion potential. However, in utility boilers, it does not pose a similar safety threat. Due to this difference, it is very important to answer questions like, How does a crack initiate? What is the crack growth rate of cracks once they initiate in a normal tube with weld attachment? How deep is a crack allowable if we know the growth rate of a given crack. Answers to these questions are important for appropriate inspection strategies as well as for removal of affected panels. However, these answers are not clear at this stage and require some focused investigation into this problem.

Eliminating stress-assisted waterside corrosion in recovery boilers would eliminate the cost of replacing boiler bottoms where waterside corrosion under external attachment welds has produced deep internal fissures. It would also eliminate the risk of tube ruptures propagating from internal cracks. This project is geared towards resolving these questions by doing appropriate research work at IPST and taking the lead to begin an organized effort, on a bigger scale, by involving experts from the pulp and paper industry and other industries, as well as other researchers such as those from Oak Ridge National Laboratory.

DELIVERABLES:

1. Report on occurrence of stress-assisted waterside corrosion in recovery boilers and on its correlation with feedwater treatment practices, chemical cleaning practices and attachment weld design. This will be done through an industry-wide questionnaire and a BLRBAC incident report summary.
2. Evaluate the effectiveness of remedial measures tested in member-company boilers. This will be done through the questionnaire by April 2000.
3. Start an MPLUS project with ORNL to do initial failure analysis to investigate any metallurgical changes associated with SAC in kraft recovery boilers. To be completed by April 2000.
4. Organize a national colloquium on SAC in recovery and other utility boilers so as to learn from the past experience of personnel involved in similar problems in other industries and also to focus our efforts to solve this problem.

STATUS OF GOALS FOR FY 1999-00:

1. Complete analysis of replies from industry-wide SAC survey and report to PAC and member companies.

2. Complete an MPLUS project with ORNL to do initial failure analysis to investigate any metallurgical changes associated with SAC in kraft recovery boilers.

3. To organize a national colloquium on SAC in recovery and other utility boilers. By August 2000.

SCHEDULE:

Task Descriptions	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
Conduct Literature Survey		---------	----------	----------X	
Prepare Questionnaire		-------X			
Send Questionnaire to Member mills		---	---------X		
Analyze results and report to PAC				----------X	
To Start MPLUS Project at ORNL			----------	--X	
Finish MPLUS				----------X	
Organize National Colloquium on SAC				----	----------X
Report to PAC					----------X

DISCUSSION:

Task I – Industry wide survey on SAC

The first task for this project is to conduct a survey of the pulp and paper industry on waterside cracking of waterwalls in kraft recovery boilers and power boilers in the industry. The questionnaire was designed to check the extent of the SAC problem in different boilers and correlate them to the process parameters, specific locations of attack, boiler water chemistry, and mitigation strategies. There is a concern that many boiler operators are not fully aware of SAC problems or are not actively inspecting their boilers to detect such problem; therefore this survey will also provide information on the level of awareness about SAC in the pulp and paper industry. The questionnaire is included in this report.

We were still receiving replies while writing this report. We expect to get most of the replies by March and start analyzing information. Data will be shared with PAC and will also be included in our next annual project review report.

Task II – Failure analysis of waterwall tubes with cracks on waterside

The main objective of this task is to perform failure analysis on waterwall tubes with cracks from the waterside. The main question is if there is any microstructural change, associated with welded tubes, which is prone to cracking. Microhardness testing will be done on tubes in the areas with and without cracks on the casing side as this will help determine any mechanical property changes associated with welding.

Major parts of this task will be carried out at ORNL, through an MPLUS project where IPST researchers will work with ORNL personnel on failure analyses waterwall tubes with SAC cracks. A member company has supplied waterwall tubes with SAC for this project. Waterwall tubes with similar cracks will also be examined at IPST using a similar approach to gather more information on metallurgical aspects of this failure. Results from these failure analyses will be compiled and presented to PAC at the next meeting.

Stress-Assisted Cracking Questionnaire

A. CONTACT INFORMATION

1. Company_____
2. Location_____
3. Contact Person_____

_____

B. BOILER DESIGN

1. Original boiler information

Boiler manufacturer_____ Boiler type_____

Field-erected or package_____ Fuel_____

Commissioning date_____ Capacity (lb fuel/day)_____

Steaming rate (design)_____ Steaming rate (average)_____

Operating pressure (design)_____ Operating pressure (average)_____

Final steam temperature_____

2. Retrofit information

Date_____ Manufacturer_____

What was done, and Why?

Answer following only if they changed after retrofit:

Capacity (lb fuel/day)_____

Steaming rate (design)_____ Steaming rate (average)_____

Operating pressure (design)_____ Operating pressure (average)_____

Final steam temperature_____

3. Retrofit information

Manufacturer_____

Date_____

What was done, and Why?

Answer the following only if they changed after retrofit:

Capacity (lb fuel/day)_____

Steaming rate (design)_____ Steaming rate (average)_____

Operating pressure (design)_____ Operating pressure (average)_____

Final steam temperature_____

C. **INSPECTION FOR WATERSIDE PROBLEMS**

1. Have cracks, fissures, or sharp grooves been detected on waterside surfaces in the economizer, generating tubing, downcomers, or any other water-wetted surfaces? ***No*** means that none was found after looking for it. ***Don't know*** means that it hasn't been looked for.

❑ Yes ❑ No ❑ Don't know

If the boiler experienced cracking at more than one place, please fill out a separate page 2 for each.

2. Defect site

❑ Windbox casing attachments
❑ Windbox extension vertical seal plate
❑ Buckstay connections to waterwalls
❑ Ash hopper seal plate
❑ Smelt spout opening
❑ Smelt spout
❑ Floor tubes
❑ Arch tubes
❑ Roof tubes
❑ Economizer tubes
❑ Steam drum
❑ Other weld attachments
❑ Mud drum
❑ Floor-to-sidewall seal
❑ Superheater screen tube tangent welds
❑ Other_____

3. How were defects detected (Mark all that apply, using numbers if there is a sequence followed)?

❑ After tube failure (visual)
❑ Radiography
❑ Visually (i.e., boroscope)
❑ Metallurgical analysis
❑ Other_____
❑ Don't know

4. Were failure modes identified as (mark all that apply):

❑ Corrosion fatigue
❑ Stress corrosion cracking
❑ Stress-assisted cracking
❑ Weld defect
❑ Other_____
❑ Don't know

5. How many tubes affected at this site.

❑ 1 ❑ 6-10 ❑ 21-50 ❑ >100
❑ 2-5 ❑ 11-20 ❑ 51-100 ❑ Don't know

6. Deepest wastage found

❑ 0-0.005 inches
❑ 0.006-0.025 inches
❑ 0.026-0.050 inches
❑ 0.051-0.100 inches
❑ >0.100 inches
❑ Through
❑ Don't know

7. Were deposits found near the defect? If so, what was deposit weight in gm/ft^2.

8. Were there any major changes in boiler operating practices prior to failure detection?

❑ No ❑ Don't know
❑ Yes (Please describe changes)

9. What is the number of normal startup/shutdown cycles experienced by the affected sites?_____

10. What is the number of trips and hot restarts experienced by the affected site? _____

11. What is the number of ESP's experienced by the affected site? _____

D. **BOILER CLEANING**

1. Number of chemical cleanings (waterside) seen by affected area_____
2. Cleaning solution

❑ Hydrochloric
❑ Chealant
❑ Other_____
❑ Don't know

3. Number of mechanical cleanings (waterside) seen by affected area
   - ❑ Water spray_____
   - ❑ Scraping or rodding_____

E. **BOILER WATER CHEMISTRY**

1. General
   - ❑ Demineralized
   - ❑ Softened
   - ❑ Other_____
   - ❑ Don't know

2. Feedwater dissolved oxygen concentration
   - ❑ 0-5
   - ❑ 6-10
   - ❑ 11-20
   - ❑ 21-50
   - ❑ 51-100
   - ❑ >100
   - ❑ Don't know

3. Boiler water treatment
   - ❑ Phosphate
   - ❑ Coordinated phosphate
   - ❑ Equilibrium phosphate
   - ❑ Chealant
   - ❑ Polymer
   - ❑ Other_____
   - ❑ Don't know

4. Oxygen scavengers
   - ❑ Sulfite
   - ❑ Ammonia
   - ❑ Hydrazine
   - ❑ Cyclohexylamine
   - ❑ Other_____
   - ❑ Don't know

5. Feedwater polishing
   - ❑ Yes
   - ❑ No
   - ❑ Don't know

6. Feedwater/Condensate system metallurgy
   - ❑ Ferrous
   - ❑ Yellow metal
   - ❑ Other_____
   - ❑ Not applicable
   - ❑ Don't know

7. Condensate polishing
   - ❑ Cationic
   - ❑ Anionic
   - ❑ Cationic/anionic
   - ❑ 100%
   - ❑ >100%
   - ❑ Not applicable
   - ❑ Don't know

8. Feedwater conductivity (microsiemens/cm):

9. If the history of the chemical treatment of the boiler is known, please include (Use a separate sheet– should include supplier/consultant, chemical treatment used, any major contamination events, etc.)

REMEDIAL ACTIONS (AFTER DEFECTS FOUND)

- ❑ Pad welding
- ❑ Dutchman
- ❑ Tube replacement
- ❑ Design Modified

F. OTHER

Information that you think is important for waterside tube failure in your boilers.

DUES-FUNDED PROJECT SUMMARY

Project Title:	**Corrosivity of Black Liquors**
Project Number:	**F037**
PAC:	**Corrosion Control**
Project Staff	
Principal Investigator:	**Preet Singh**
Co-Investigators:	**Greg Fonder**
Research Support Staff:	**Jamshad Mahmood**
PAC Subcommittee	**N/A**
FY 99-00 Budget:	**$87,601**
Allocated as Matching Funds:	**0%**
Time Allocation:	
Principal Investigator:	**17%**
Co-Investigators:	**10%**
Research Support Staff:	**65%**
Supporting Research:	
Special Students:	**Adolfo Anaya (M.S. thesis)**
External (Where Matching Is Used):	

RESEARCH LINE/ROADMAP:

Research Line #9 - Reduce lifetime costs of construction by 30% through innovative technologies

PROJECT OBJECTIVES:

1. To characterize black liquors and relate corrosivity of different black liquors to their inorganic as well as organic compositions.
2. To investigate the role of pulped wood species pulped and their effect on the corrosivity of black liquors.
3. To relate stress corrosion cracking susceptibilities of various commonly used alloy materials with black liquor composition and temperature.
4. To participate in a larger "digester project" funded by DOE at ORNL.

BACKGROUND:

Corrosion of digesters, auxiliary equipment in contact with liquors, and storage tanks is a continuing problem in pulp mills. Some of these problems are related to the changes in the processes, whereas others are due to a lack of knowledge in predicting corrosivity of a given black liquor. Certain black liquors are considerably more corrosive than others. Although the role of inorganic constituents has been related to corrosion in laboratory

tests, the role of wood extractives and other organic constituents of black liquors has not been systematically explored. There are indications that the corrosivity of black liquors is related to the wood species being pulped. Quantification of the role of significant organic and inorganic constituent of the black liquor will help in corrosion prediction based on liquor analysis. Further, corrosion mitigation strategies can be applied to control this corrosion in digesters, storage tanks and heat exchangers, etc. For example, materials selection can be based on the wood species being pulped in a given mill.

DELIVERABLES:

1. Predict corrosion of different commonly used alloys in equipment like digesters, storage tanks, etc., handling different types of black liquor.

2. Provide mitigation strategies for the equipment handling different black liquors.

3. Predict stress corrosion cracking susceptibility of commonly used alloys in kraft digesters in different black liquor compositions and temperatures so as to avoid unexpected failures.

GOALS FOR FY 1999 00:

1. Start experimental work on correlation of black liquor constituents, both organic and inorganic, to the corrosivity of selected black liquors.

2. Investigate performance of different commonly used alloys in selected black liquors representing different wood species and pulping conditions.

3. Start experimental work to investigate the effects of black liquor composition and temperature on stress corrosion cracking of commonly used alloys in kraft digesters.

SCHEDULE:

Task Descriptions (example)	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
Install pilot digester for corrosion			----------	-----X	
Modify Digester to install corrosion probes				------X	
Meet with ORNL to collaborate on their project			----X		
Install Autoclaves		---	----------X		
Experiments in Black Liquor				----------	----------X
Report to PAC					Fall 2000

DISCUSSION:

Task I – Tests for Corrosivity of black liquor

Main objective of this task is to start a test program and investigate the effect black liquor compositions on corrosivity of black liquor. To carry out this task, we had to acquire two new autoclaves. Autoclaves are 3liter, 2205 duplex stainless steel capable of handling temperatures up to 600°F and 3000psig. These autoclaves have been tested and are being used for preliminary tests.

A pilot digester was donated to IPST by The Proctor and Gamble Company. This digester will be dedicated to corrosion studies only. Digester has been commissioned and is being modified to accommodate corrosion monitoring during cooking cycles.

Task II – Participation in ORNL "Digester Project"

Objective of this task is leverage dues funded project activities by participating in ORNL "digester corrosion" project. This DOE funded project is aimed at digester corrosion and involves various research groups and other collaborators from the pulp and paper industry and equipment manufacturers. First meeting was held in Tacoma, WA. Any significant activity on this project has not started yet, but we are worked with ORNL group and identified different areas where we will participate in this project. We will report on further activities to the PAC in Fall 2000 and report to the member companies in next annual project review report.